VOL. LIII, NO. 4, APRIL, 1958

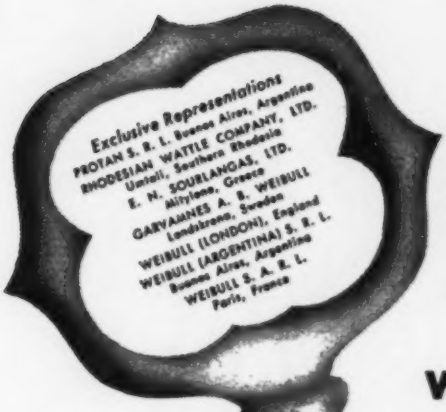
THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLISHED MONTHLY BY
THE AMERICAN LEATHER CHEMISTS ASSOCIATION
PUBLICATION OFFICE, EASTON, PA.

Fifty-fourth Annual Meeting

May 25 - 28, 1958

New Ocean House, Swampscott, Mass.



YOUR KEY

to Reliable, Direct Continuous World-Wide Sources for

VEGETABLE TANNING MATERIALS

QUEBRACHO
Products of the
FORESTAL
Group

"SUPERIOR" Ordinary
"SUPERIOR" Clarified
"SUPERIOR 350"

WATTLE EXTRACT BRANDS

"RHOMOSA" - So. Rhodesian
"WEIBULL" - East African
"NCS" - South African

QUEBRACHO EXTRACTS

"Z" Brand
"ZORCAL" Brand
"LUTECIA" Brand
"F.A." Brand

WATTLE BARK
CHESTNUT EXTRACT
VALONEA EXTRACT
MYRABOLAMS
MYRABOLAM EXTRACT
MANGROVE BARK
AND EXTRACT
SUMAC
DIVI DIVI
OAKWOOD EXTRACT

World-wide
Buenos Aires
London • Paris
Landskrona
Bombay • Calcutta
Durban • Umtali
Mitylene • Palermo
Rio de Janeiro

The **OLSON**
IMPORTING COMPANY Inc.
20 VESEY STREET, NEW YORK 7, N. Y.
Cable Address "Carosage"
Tel. WOrth 4-4084

se, Swampscott, Mass.

The Journal
of the
AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII APRIL 1958 No. 4

CONTENTS

The Reaction of Some Thiocyanato-Chromiate Complexes with Collagen. I. The Reinecke Salt - - - - - - - - - - - - *By* K. H. GUSTAVSON 192

Determination of N-Terminal Amino Acids of Collagen by the 2,4-Dinitrofluorobenzene Method - - - - - - - - - - - - - *By* C. DEASY 203

Life Lines - - - - - - - - - - - - - 209

ALCA News - - - - - - - - - - - - - 210

Abstracts - - - - - - - - - - - - - 224

SUBSCRIPTION - - MEMBERS $12.00 A YEAR - - NONMEMBERS $15.00

Published Monthly by

The American Leather Chemists Association

Entered as Second-Class Matter at the Post Office, Easton, Pa.
Acceptance for mailing at special rate of postage as provided for in section 1103.
Act of October 3, 1917, authorized July 16, 1918

COPYRIGHT, 1958, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices and Plant
ERIE, PA.

There's More-Much More

to choose from

Extracts and Raw Tanning Materials
From the Most Complete Line of Brands

QUEBRACHO

Ordinary	Clarified
Formosa	Bestsoubi
Granchaco	Horsehead
Guarani	Rex
India	Avion
Sastre	Sol Puma
F. A.	
La Galera	
Puma	

CHESTNUT

Progil S. A.	Tanins Rey
Lion's Head	Bull Head

WATTLE

S. African	E. African
H. E. C.	Rhino
N. C. S.	

★

SPECIAL SPRAY DRIED EXTRACTS

Driton, R. W. D. — Quebracho • Valonia • Myrabolams • Mangrove • Blends

Myrabolams, Divi-Divi, Mangrove, Valonia, Sumac and Other Vegetable Tanning Materials from All Parts of the World.

TANIMEX CORP. — ELKAN-RIVER PLATE CORP.

27 William Street • New York 5, N. Y.

WHitehall 3-6300

To Prevent Spoilage

USE.. BSM-II

as part of Good housekeeping practice

Starch and protein finishing materials provide a fertile substrate for the growth of microorganisms.

BSM-11 is an effective economical preservative providing outstanding control with a synergistic combination of bactericides and fungicides.

Our representative will give technical advice on the most efficient solution of your microorganism control problems.

BUCKMAN

Laboratories, Inc.

Manufacturing Chemists • Memphis 8, Tennessee

Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS

"I contemplate with pride the way they'll tan my hide-with Chestnut"!

The quality and economy of *European Chestnut Extracts* are the result of years of research and expanding facilities in more than 60 factories throughout France, Italy and Switzerland.

QUALITY...

Manufactured according to the most modern and highest standards, *Chestnut Extract* is a guarantee of perfect uniformity of quality and color in the finished leather.

Leather tanned with *Chestnut Extract* does not oxidize, has pleasant color, and will not darken when exposed to light or time.

Leather tanned with *Chestnut Extract* has definitely a better wearing resistance.

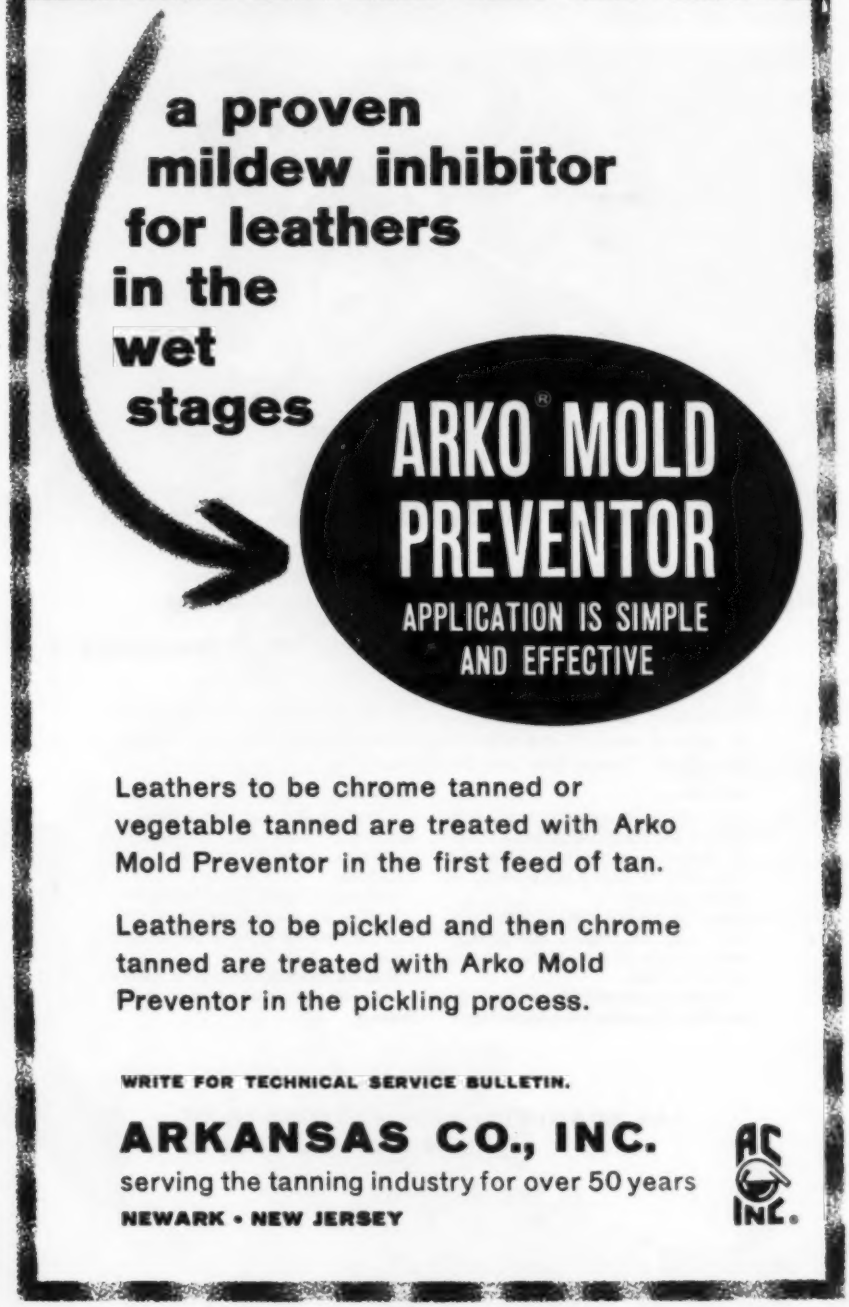
ECONOMY...

Chestnut Extract is delivered in spray-dried form, cold water-soluble and ready to use. There is no cost of dissolving.

Chestnut Extract gives free acidity ... makes unnecessary costly and difficult additions of acids to the tanning liquors.

It is the cheapest way to good leather ... provides the highest yield in the tannery.

The EUROPEAN MANUFACTURERS OF CHESTNUT EXTRACTS


a proven
mildew inhibitor
for leathers
in the
wet
stages
ARKO® MOLD
PREVENTOR
APPLICATION IS SIMPLE
AND EFFECTIVE
Leathers to be chrome tanned or vegetable tanned are treated with Arko Mold Preventor in the first feed of tan.
Leathers to be pickled and then chrome tanned are treated with Arko Mold Preventor in the pickling process.
WRITE FOR TECHNICAL SERVICE BULLETIN.
ARKANSAS CO., INC.
serving the tanning industry for over 50 years
NEWARK • NEW JERSEY
AC INC.

JACQUES WOLF CHEMICALS Produce High Grade Leather

SYNEKTAN 0-230*—For use alone or in combination tanning with vegetable extract or chrome. Useful for rapid tannages and bleaches. Excellent as a retan on chrome stock.

SYNEKTAN 0-272*—Similar to Synektan 0-230 in use. Produces smooth grain leather with mellow feel.

SYNEKTAN NPP*—For high grade white leather of improved light-fastness. Also used in combination with Alum, Chrome, and in producing pastel shades. Produces full, soft leather of good weight.

SYNEKTAN NCRP*—Recommended for Sport goods, Suede and Elk leathers. Produces full, plump, fine grained leather, of good tensile strength.

FAT LIQUORS—For all types of leather. Special quality fat liquors with high lubricant effects and excellent light fastness for whites.

TANASOL PW*—Syntan in beads, to use with Tanasol NCO for bleaching chrome stock and in retanning chrome stock. In the lye bath for good level colors.

TANASOL NCO*—Syntan in beads, to use with extracts in the tanning and retanning operations.

FUNGIZYME* BATES—Pancreatic bating salts of standard, controlled quality.

BATE A & AS—For sheep skins and sole leather.

BATE B & BS—For furniture leather, side leather and calf skins.

SULPHONATED OILS—(Various Bases.)

MONOPOLE OIL*—(For Finishing.)

EMULSIFIERS AND DETERGENTS—For good degreasing.

Samples and information upon request.

JACQUES WOLF & CO.
Chemicals **PASSAIC, N.J.**

***Plants in:* Clifton, N.J., Carlstadt, N.J., Los Angeles, Calif.**

* Reg. U. S. Pat Office

New PRIMAL finish

adds that quality touch!

Newly-developed Rohm & Haas PRIMAL white finish is particularly excellent for the quality finishing of smooth white side leather for shoes and handbags.

This PRIMAL white finish contains a special new pigment grind as well as new binders. The advantages of using PRIMAL white finish for shoe and handbag leather are important, for PRIMAL white finish provides

- Better flexibility
- Greater resistance to washing—without the use of lacquers
- Excellent flow-out—it spreads easily sideways with virtually no streaking
- Good coverage or hiding power—usually requires fewer coats

It may pay you to investigate this new PRIMAL white finish for your particular needs. For further information about PRIMAL white finish and other leather chemicals and services, simply write to Leather Chemicals Department or get in touch with your Rohm & Haas representative.

Chemicals for Industry

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries

PRIMAL *is a trade-mark, Reg. U.S. Pat. Off. and in principal foreign countries.*

Consult

RESEARCH *and* **TECHNICAL DEVELOPMENT SERVICE**

about your

Tanning, Dyeing, Processing

and **Finishing** *problems*

Geigy products are carried in all important tanning centers

GEIGY DYESTUFFS *division of Geigy Chemical Corporation*
Saw Mill River Road, Ardsley, New York

200 years Geigy

BRANCH OFFICES: *New England: Newton Upper Falls, Mass. Charlotte, N. C. • Chattanooga • Chicago • Los Angeles Philadelphia • Portland, Ore. • Toronto*
In Great Britain: *The Geigy Co., Ltd., Manchester*

gdc
QUALITY DYESTUFFS

QUALITY DYESTUFFS

FOR ALL LEATHERS BACKED BY PROMPT TECHNICAL SERVICE

From Research to Reality

gdc gaf

GENERAL DYESTUFF COMPANY

A DYER DIVISION OF

GENERAL ANILINE & FILM CORPORATION

435 HUDSON STREET • NEW YORK 14, NEW YORK

CHARLOTTE • CHATTANOOGA • CHICAGO • LOS ANGELES • NEW YORK • PHILADELPHIA • PORTLAND, ORE.
PROVIDENCE • SAN FRANCISCO • IN CANADA: CHEMICAL DEVELOPMENTS OF CANADA, LTD., MONTREAL

FIRST WITH MANY NEW DEVELOPMENTS

"FORESTAL"

are now pioneering the manufacture of

SPRAY-DRIED POWDERS

AT SOURCE

QUEBRACHO
from
ARGENTINA

"CROWN"
and
"CROWN 350 GS"

- **Improved Colour**
- **Improved Tanning Quality**
- **Readily Soluble**—*can be added direct to pits or vats—and specially effective in drums*
- **Easily Handled**—*does not adhere to bags*

THE FORESTAL LAND, TIMBER & RAILWAYS CO., LTD.

SHELL-MEX HOUSE, STRAND, LONDON W.C. 2

Telephone: COvent Garden 2211 • Cables: Forestimba, London • Telex: 2-2576

SOLE SELLING AGENTS IN UNITED STATES AND CANADA

BARKEY IMPORTING CO., INC.

44 EAST 53rd ST., NEW YORK 22, NEW YORK

SODIUM SULFIDES

One good gauge of their purity is your shoe

A mathematician friend tells us the probability is that one of the shoes you are wearing was treated with a Hooker sulfide.

He bases his conclusion—faulty, perhaps, but thought-provoking—on the fact that more than 50% of American leather is unhaired with Hooker sodium sulfide or sodium sulfhydrate.

Why so much? Three reasons:

1. *Hooker specifications*

SODIUM SULFIDE

Na_2S .....60 to 62%	NaCl ..... 1.5% Max.
Water of Crystallization 35% Min.	Fe ..... 8 ppm Max.

SODIUM SULFHYDRATE

NaSH 70-72%	NaCl ..... 0.8% Max.
Water of Crystallization 26% Min.	Fe ..... 5 ppm Max.

2. *Hooker packaging*

Hooker sodium sulfide and sulfhydrate *always* come to you in brand-new drums with an inert lacquer lining that prevents iron pickup. The drum lids are secured airtight with six sturdy lugs to prevent air and moisture contamination.

3. *Hooker flakes*

You get clean, firm flakes that dissolve rapidly into process without stirring or decanting.

For complete specifications on Hooker sodium sulfide and sulfhydrate, write for technical data sheets.

HOOKER ELECTROCHEMICAL COMPANY
904 UNION STREET, NIAGARA FALLS, N. Y.

Niagara Falls Tacoma Montague, Mich. New York Chicago
Los Angeles Philadelphia Worcester, Mass.
In Canada: Hooker Chemicals Limited, North Vancouver, B. C.

HOOKER CHEMICALS PLASTICS

famous

TANNERY

"HOUSEHOLD NAMES"

Every industry has its famous names. In tanning, Atlas, and the products it has developed through the years, all are "household names"—respected because they represent the finest of their kind and for their purposes.

How many of those names do you recognize as "old friends?" How many of the new ones are you familiar with?

Atlas, keeping apace of, and frequently leading the way to, new progress in tanning, brings you the products best suited to your needs.

It is a fact that when tanners change to Atlas Fatliquors, few ever change again.

Atlas **REFINERY, INC.**

142 LOCKWOOD STREET

NEWARK 5, N. J.

For better SOLIDS PASTELS WHITES

neutralize your leathers with SOLVAY AMMONIUM BICARBONATE

For finer, truer tones in solids, pastels and whites, leathers *need* the superior neutralizing action of SOLVAY Ammonium Bicarbonate. It penetrates deeper and is milder—pH is only 7.8. This superior neutralization helps produce better quality leather and makes possible deep and uniform penetration of dyes. And SOLVAY Ammonium Bicarbonate can be used in an economical 1½% solution. For extra savings, order in 100-lb. vapor-barrier bags.

For sample, write your nearest SOLVAY office.

OTHER PRODUCTS FOR TANNERS

Solvay Cleansing Soda X
Mutual Boreon Mound X
Solvay Cleansing Soda XX
Mutual Sodium Bichromate
Solvay Snowflake® Crystals
Mutual Potassium Bichromate

SOLVAY®

SOLVAY PROCESS DIVISION

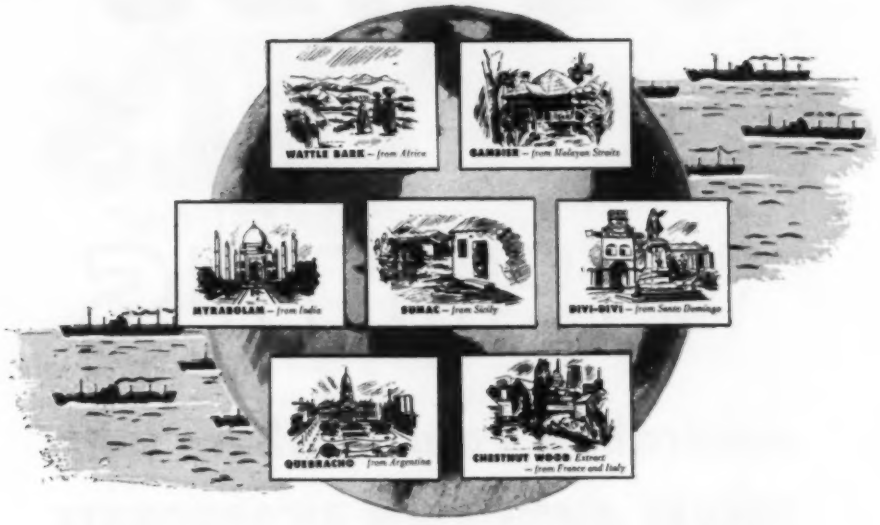
Allied Chemical

ALLIED CHEMICAL & DYE CORPORATION
61 Broadway, New York 6, N. Y.

BRANCH SALES OFFICES:
Boston • Charlotte • Chicago • Cincinnati • Cleveland
Detroit • Houston • New Orleans • New York • Philadelphia
Pittsburgh • St. Louis • Syracuse

ONE OF AMERICA'S FOREMOST IMPORTERS, PROCESSORS and MANUFACTURERS OF

Tanning and Dyewood Extracts


WATTLE BARK — from Africa
GAMBIER — from Malayan Straits
MYRABOLAM — from India
SUMAC — from Sicily
DIVI-DIVI — from Santo Domingo
QUEBRACHO from Argentina
CHESTNUT WOOD Extract — from France and Italy

With 88 years of continuous service to the tanning and dyeing industry, the J. S. YOUNG CO. has progressively expanded its facilities... anticipating the requirements of the entire industry... large and small operators, alike. We are importers, processors and manufacturers of practically every well-known, reputable tanning extract and dyewoods—for all branches of the industry... for leather, and for silk, wool and synthetic textiles. Our facilities have grown in capacity, flexibility and efficiency. Our skilled technicians and research facilities are at the service of the industry to help meet and solve individual problems... to meet your specifications and requirements.

Your dependable source of supply, always!

Manufacturers of the famous CHEMBARK natural Tanning Extracts for the CHEMTAN CO.... and other special products.

The J. S. YOUNG CO.

2701-2755 Boston St., Baltimore 24, Maryland

Experienced technical advice available on request from Baltimore or any of our branches:

PHILADELPHIA • DANVERS, MASS. • PEABODY, MASS. • NEW YORK • CHICAGO • MILWAUKEE

How Mobil Blends Economy into Fatliquors!

THROUGH blending petroleum chemicals with normal fatty oils and greases, Mobil has achieved fatliquors of the highest efficiency and the lowest possible cost. Here is one example.

Mobiltan O, as a result of the Mobil petroleum chemicals it contains, has these desirable characteristics: Low moisture content . . . high resistance to oxidation . . . complete freedom from spue-forming tendencies. Yet it is one of the lowest cost fatliquors offered to the tanning industry.

Mobil has a wide range of tanners products . . . each one designed to help you make better leather, *cheaper!*

There's a right Mobil product for your every tanning need

MOBILKOR—identifies a complete line of stuffing greases for use on heavy leathers, as well as work-shoe upper leathers.

MOBILSET—is the new trademark for our highly nourishing leather oils for inclusion as fatliquor additives or as finishing oils.

MOBILCROME 1—identifies a one-bath product for economical chrome tanning of all leathers.

MOBILTAN—indicates products specifically designed for application on all fatliquored leathers.

MOBILON—individually designed formulations for sole waterproofing, sponging and washing compounds.

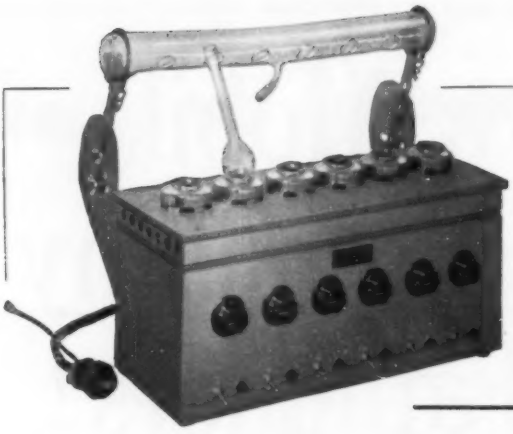
For complete technical data on products of any of the above product groups write, **Socony Mobil Oil Co. Inc., Tanners Division • 150 E. 42nd St., N.Y. 17, N.Y.**

Mobil

Socony Mobil

First choice of Tanners since 1866

Socony Mobil Oil Company, Inc., Tanners Division, 150 E. 42nd St., N. Y. 17, N. Y.



High temperatures—up to 450°C

Six separately controlled heaters

Takes flasks 10 to 100 ml

Corrosion-resistant

Thomas — LABCONCO HIGH TEMPERATURE KJELDAHL DIGESTING APPARATUS

With six 200-watt heaters, each with separate rheostat control, pilot lamp and "on-off" switch, for completely independent operation at temperatures up to 450°C. Stainless steel housing is 19⅛ inches long × 7⅝ inches deep × 10³⁄₁₆ inches high to tops of heaters. Finish is corrosion resistant throughout. Fume duct is of Pyrex brand glass and in accordance with *"Recommended Specifications for Microchemical Apparatus,"* A.C.S. Committee for the Standardization of Microchemical Apparatus; see *Analytical Chemistry, Vol. 23, No. 3 (March, 1951), p. 52A*. Accommodates Kjeldahl flasks 10 ml, 30 ml or 100 ml capacity, making the apparatus suitable for micro or semimicro analysis.

Disc-shaped heaters embedded in refractory cement are spaced 3 inches from center to center on transite top and are separated from controls by a ventilated air chamber. Stainless steel heater tops have a 26 mm diameter opening to take 30 or 100 ml Kjeldahl flasks. Readily insertable wire gauze discs are available for use in heater tops for supporting 10 ml Kjeldahl flasks or tubes less than 26 mm in diameter.

Control knobs and switches are insulated by a transite panel from the rheostats mounted in ventilated rear compartments. Fume duct, 516 mm long × 51 mm outside diameter, has six openings 22 mm diameter for flask necks and drains through ⅛ inch o.d. center outlet tube. Fume duct is supported by two slotted aluminum clamps attached to wing-shaped brackets at rear corners of housing. Flexible arrangement of clamps permits easy adjustment for flasks or test tubes up to 12 inches long at any desired angle.

7498-E. Kjeldahl Digesting Apparatus, Micro, Thomas-Labconco, Electric, as above described, with six independently controlled 200-watt heaters. Complete with six heater tops for 30 or 100 ml Kjeldahl flasks, fume duct of Pyrex brand glass, two clamps with locking bolts to support duct, and 4 ft., 3-wire connecting cord with 2-prong attachment plug cap and grounding tail. For use on 115 volts, a.c. or d.c. Maximum power consumption 1200 watts. **242.25**

More detailed information sent upon request.

A.H.T.CO. QUALITY AND SERVICE PHILA. U.S.A. LABORATORY APPARATUS

ARTHUR H. THOMAS COMPANY

More and more laboratories rely on Thomas / Laboratory Apparatus and Reagents

VINE ST. AT 3RD • PHILADELPHIA, PA.

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII APRIL 1958 No. 4

DR. HENRY B. MERRILL - - - - - - - - - - - - *Editor-in-Chief*
B. D. Eisendrath Tanning Co., Racine, Wisconsin

DR. THOMAS C. THORSTENSEN - - - - - - - - - - *Associate Editor*
Lowell Technological Institute Research Foundation, Lowell, Massachusetts

EARL J. WATT - - - - - - - - - - - - - - - *Managing Editor*
Lowell Technological Institute, Lowell, Massachusetts

EDITORIAL BOARD

E. D. Compton, Eagle-Ottawa Leather Company
J. H. Highberger, United Shoe Machinery Corporation
Joseph R. Kanagy, National Bureau of Standards
Mieth Maeser, United Shoe Machinery Corporation
William T. Roddy, Tanners' Council Research Laboratory
Carl G. Telander, Raser Tanning Company
Thomas C. Thorstensen, Lowell Technological Institute Research Foundation
H. G. Turley, Rohm & Haas Company
Ralph H. Twining, L. H. Lincoln & Son, Inc.
C. David Wilson, Fred Rueping Leather Company
Wallace Windus, Eastern Utilization Research and Development Division, United States Department of Agriculture

ABSTRACTERS

Jose Behar B.
Margam G. Behar
Theodore D. Braunschweig
G. A. Bravo
James M. Cassel
Ira D. Clarke
Jerome Jansing
Henri Krakowski
Robert M. Lollar
Liboslav Masner
Ralph H. Twining
J. F. Wagoner
Harry R. Wilson

All manuscripts should be sent to the Editor-in-Chief, 1012 College Avenue, Racine, Wisconsin.

Mail in reference to subscription, advertising, and other business should be addressed to the Secretary-Treasurer of the Association. Checks should be made payable to the American Leather Chemists Association.

General correspondence concerning the *Journal* should be mailed to the Managing Editor.

Subscriptions—$12 per year for members; $15 for nonmembers.

THE REACTION OF SOME THIOCYANATO–CHROMIATE COMPLEXES WITH COLLAGEN
I. THE REINECKE SALT

K. H. GUSTAVSON

Garverinäringens Forsknings Institut
Stockholm, Sweden

ABSTRACT

The Reinecke salt, $[Cr(CNS)_4(NH_3)_2] \cdot NH_4 \cdot H_2O$, reacts irreversibly with collagen, raising the shrinkage temperature by as much as 25 °C. The reaction is, however, a very slow one, and the chromium complex that is fixed contains only two CNS groups per Cr. This indicates that tanning does not occur until part of the CNS groups have been displaced from the complex, probably by water molecules. Tanning experiments with different modified collagens indicate that the altered Reinecke salt is fixed chiefly by the guanidine group of the arginine residue.

INTRODUCTION

A number of chromium complexes, particularly oxalato and thiocyanato compounds, have been studied and used for separation of individual amino acids present in protein hydrolyzates. Max Bergmann was particularly interested in the specificity of such complexes for a number of amino acids. Thus, Bergmann and Fox (1) found that trioxalatochromiate forms with glycine, in the presence of hydrochloric acid in water-alcohol solution, two well-crystallized double salts containing both glycinium and potassium as cations. Thus, the complex $[Cr(C_2O_4)_3]_6K_{12}$ $[HOCO \cdot CH_2 \cdot NH_2]_6 \cdot 3H_2O$ is formed when the oxalatochromiate is in excess of the glycine. The potassium *trans* dioxalatochromiate gives with glycine another type of complex, with glycine inside the chromium complex (2). From hydrolyzates of gelatin and collagen only glycine was precipitated by the trioxalato complex. This compound appears to be specific for glycine under the experimental conditions used by Bergmann and Fox (1). Among a number of other chromium compounds investigated as amino acid precipitants the thiocyanatochromiates should be especially noted, since they have found use as reagents for the estimation of proline and hydroxyproline, two amino acids of great importance for collagen. Reinecke's salt, $[Cr(CNS)_4(NH_3)_2]$ $NH_4 \cdot H_2O$, was used by

Kapfhammer and Eck (3) as early as 1927 for the simultaneous precipitation of these two amino acids present in gelatin hydrolyzates. Since arginine also reacts with the Reinecke salt, forming a type of the Morland salt, the guanidinium complex (2), the arginine has to be removed, usually by flavianic acid previous to the addition of the Reinecke salt. In further work Bergmann (4) studied modified Reinecke salts as amino acid reagents, particularly those containing amines other than ammonia, e. g., two aniline groups, such as in tetrathiocyanato-dianilidochromiato acid ("rhodanilic acid"). The ammonium salt of this compound is an efficient precipitating agent for proline even in the presence of hydroxyproline, for instance in collagen hydrolyzates. The hydroxyproline is subsequently precipitated with the Reinecke salt in the hydrolyzate freed from proline.

In connection with studies of the reaction of the hydroxyproline residue in collagen, particularly the reactivity of the hydroxy group (5), the interaction of thiocyanatochromiates with collagen has been investigated. Although the reaction of the Reinecke salt with collagen did not give an explicit result as to the reactivity of the hydroxyproline residue, the findings appear to be of general interest since they exemplify the versatility of chromium compounds in their reaction with and fixation by collagen.

In their comprehensive survey of the tanning action of a great number of chromium compounds, mainly uncommon ones, Stiasny and Lochmann (6) included the Reinecke salt. It was found to possess some affinity for collagen but increased its hydrothermal stability very slightly; hence, they did not consider it to be a tanning agent. Their findings will be discussed later on.

In an earlier paper (7) the interaction of potassium hexathiocyanatochromiate, $K_3[Cr(CNS)_6]$, with collagen in aqueous and alchoholic solutions has been investigated. The main findings were as follows: The hexathiocyanate compound is originally taken up by collagen in the form of the intact $[Cr(CNS)_6]^{3-}$ complex. The main part of the complexes removed by collagen is present as an adsorption compound, and only about one-third of the total amount of chromium sorbed by the collagen is irreversibly fixed. This attachment does not result in stabilization of the protein. Actually the reverse occurs, as shown by a decrease of shrinkage temperature determined by the "shocking" method, probably caused by the rupture of salt-like links in the collagen lattice by the chromium complex attached to the cationic protein groups. By washing of the stock, or by slowly heating the stock in water, CNS groups are removed from the fixed chromiato complex. Probably aggregation of the chromiate takes place through the introduced hydroxy groups with a subsequent multipoint fixation of the enlarged complexes by collagen, resulting in shrinkage temperature increase. Upon long periods of tanning in aqueous solution, exposed to daylight, the hexathiocyanate complex is similarly decomposed, and tanning takes place *in situ*. This effect is also evident from the improved tryptic resistance of the chromed collagen.

It is of interest to note that polyamide (Igamid 6A) is destroyed in solutions of the hexathiocyanate compound, and that codskin loses a great deal of its mechanical strength after fixation of the hexathiocyanatochromiate.

EXPERIMENTAL

The procedure of Kapfhammer and Eck (3) was followed for the preparation of the Reinecke salt, $[Cr(CNS)_4(NH_3)_2]\ NH_4 \cdot H_2O$. This consists essentially of melting together ammonium thiocyanate and ammonium bichromate. Lyon hide powder and isoelectric calfskin pelt served as substrates. The modified specimens of collagen have been described in earlier papers. They were: (*a*) Deaminated (8), (*b*) N-acetylated (9), (*c*) O-acetylated (9), and (*d*) esterified (methylated) (10) collagens. A specimen of guanidinated collagen, in the form of hide powder treated with O-methyl-*iso*-urea (11) in order to convert the ϵ-amino groups of the lysine residues into arginine groups, was also studied. It contained 0.76 meq. guanidyl groups per gram of collagen. Hide powder and pelt treated for 7 days in 0.3 and 0.5 *M* solutions of sodium periodate were included in the study, as well as hide powder which had been heat-denatured by immersion in water at 70°C. for one minute. Further specimens of hide powder with its ionic groups completely inactivated by irreversibly fixed lignosulfonic acid (12), trinaphthalene-dimethylene-disulfonic acid (13), and a Novolak sulfonic acid, were investigated, as well as wattle-tanned hide powder with a degree of tannage of 64.

The preparation of the Reinecke salt, $[Cr(CNS)_4(NH_3)_2]\ NH_4 \cdot H_2O$, contained 14.7% Cr, 27.8% total N, 11.8% ammonia N, and 36.1% S, which figures are in satisfactory agreement with the calculated values. The total N, estimation of which by the Kjeldahl and Dumas methods has been reported to give highly erratic values (6), was determined by the Kjeldahl technique, using, for the digestion of 100 mg. of the Reinecke salt, 25 mg. of selenium, 2.5 g. anhydrous sodium sulfate, and 5 ml. sulfuric acid (sp. gr. 1.84) for 30 minutes. Consistent values close to the theoretical one were obtained. Kapfhammer and Eck (3) also found that the Kjeldahl method yields correct values for the total N content.

On paper ionophoresis (14) of the freshly prepared 1.0% aqueous solution of the Reinecke salt, the main part of the chromium complexes carried a negative charge, although on aging of the solution nonmigrating chromium complexes became prominent.

As to the analytical details, the estimations of total nitrogen and collagen deserve comments. As already mentioned, the total N was determined by the Kjeldahl method. The modification of this method used gave 27.8% total N in the Reinecke salt, which is identical with the theoretical value.

The total sulfur content was determined by oxidation of the Reinecke salt with sodium peroxide (15). From the total sulfur content, corrected for protein S which was 0.3% S on the weight of collagen, the number of CNS

groups present per atom of Cr in the chromiato complex fixed by collagen was ascertained. From this figure the percentage of N introduced in the form of the thiocyanato complexes was obtained. The total nonprotein N present as CNS and as ammonia (2 NH_3 per each Cr) was subtracted from the total N figure, giving the percentage of protein N and thus the collagen content (N $\times$ 5.56). In the following an example of the details of these operations will be given.

The Reinecke salt was used in 2.0% aqueous solution (=3.0 g. Cr per l.) at an initial pH of 4.8–5.0 and in methanol solutions containing 5.0 and 10.0% Reinecke salt (7.4 and 14.8 g. Cr per l. respectively). Portions of hide powder and calfskin pelt equal to 1.0 g. of collagen were shaken with 40.0 ml. of the aqueous solution and with 20.0 ml. of the methanol solution for 14 days. The collagen and calfskin specimens used in aqueous systems were hydrated prior to use. The stock treated in the water solution of the chromiate was freed from sorbed chromium by washing and drumming with water. The specimens from the methanol bath were extracted with methanol in order to remove uncombined chromium compounds. The shrinkage temperature of the tanned pelt was determined by (*a*) the "shocking" method (16), including strips taken from the pressed (*not* washed) specimens directly out of the tan bath, and (*b*) the ordinary method, which is characterized by slow heating of the water, commencing at 20°C. and raising the temperature 3°C. per minute, methanol extracted specimens being used.

RESULTS

Some typical results are shown in the following tables. Table I gives the data from series with hide powder treated for 14 days in 2.0 and 1.6% aqueous solutions of the Reinecke salt. The 2.0% solution is practically saturated at the temperature employed, 20°–22°C.

The percentage of collagen has in some instances (marked with an asterisk) been calculated indirectly, using the equation: % collagen = 100 — (6,4 $\times$ % Cr), the figure for Cr being based on the dry substance. This approximate equation has been derived from the figures of the direct estimation of total N, nonprotein N, and the sulfur and Cr contents of the stock.

In contrast to the reaction of the ordinary cationic sulfates and chlorides of chromium with collagen, the fixation of the Reinecke salt by collagen from aqueous solution is very slow, requiring weeks for the attainment of the maximum uptake of chromium. This slow rate of reaction is very likely due to the weak affinity of the original complex for collagen. Only after the formation of secondary products, made evident by the loss of CNS groups from the complex, are favorable conditions for the tanning process created. These alterations occur rather slowly. This is brought out by the fact that hide powder treated with ordinary basic chromium sulfate at room temperature will, as a rule, fix an amount of chromium equal to about 80% of its

TABLE I

FIXATION OF REINECKE SALT BY COLLAGEN FROM AQUEOUS SOLUTION

No.	Substrate	Final pH	% on Dry Substance			% Cr Fixed by Collagen	Ratio of CNS: Cr of Fixed Cr Compound
			Cr	S	Collagen		
Initial concentration: 3.0 *g/l Cr* (2.0% *solution*)							
1.	Hide powder (H.P.)	4.7	3.5	4.3	77	4.5	2.0 : 1.0
2.	N-acetylated H.P.	4.8	3.6	4.4	76	4.7	2.0 : 1.0
3.	N- and O-acetylated H.P.	4.6	2.7	–	83*	3.3	–
4.	Deaminated H.P.	4.6	2.7	–	83*	3.3	–
5.	Guanidinated H.P.	4.8	3.7	–	76*	4.8	–
Initial concentration: 2.0 *g/l Cr* (96 *hr.*)							
6.	Hide powder (H.P.)	4.7	3.0	–	81*	3.7	–
7.	Heat-denatured H.P.	4.8	3.5	–	77	4.5	–
8.	Calfskin pelt† (4 weeks)	5.2	4.2	4.8	73	5.8	–

*% collagen calculated from the Cr content.
†Δ Ts was + 20°C. by the shocking technique, and by the ordinary method +27°C. By "ΔTs" is meant the difference between the shrink temperatures of the calfskin pelt before and after treatment.

TABLE II

TIME FACTOR IN THE FIXATION OF REINECKE SALT BY COLLAGEN

(*1.0 g. of collagen, in the form of hide powder, treated for the periods given with 20 ml. of 2.0% aqueous solution of the Reinecke salt.*)

No.	Time of Treatment	% Cr Irreversibly Fixed, on the Weight of Dry Substance
1	1 hr.	0.2
2	4 hr.	0.3
3	8 hr.	0.3
4	24 hr.	0.5
5	48 hr.	1.1
6	7 days	2.2
7	21 days	5.8

combining capacity in 4 hr., whereas not more than 5% of the maximum fixation is attained by the Reinecke salt in aqueous solution during the same period of time under like experimental conditions. This is shown in Table II.

No chromium was fixed by either the hydrated polyamide Igamid 6A (17) or by the sodium salt of Amberlite IRC50 equilibrated at pH 6.0 (18) when these substrates were treated for 48 hr. with a 2.0% aqueous solution of the

Reinecke salt. Thus, hydrogen bonding of the Reinecke salt by the -CO·NH- links of collagen and reactions on its carboxyls are not indicated to be involved.

Further, hide powder which had its ionic groups irreversibly inactivated by trinaphthalenedimethylenedisulfonic acid (13), containing 25.8% fixed sulfo acid on the basis of collagen, combined with only .08% Cr, on the weight of collagen, in a treatment corresponding to that of specimen No. 1 in Table I. By the corresponding elimination of the acid-binding capacity of the collagen by irreversible fixation of the high-molecular α-fraction of lignosulfonic acid (12), the resulting specimen fixed only 0.5% Cr, on the basis of collagen. In both these instances all the cationic (basic) protein groups—the ε-amino groups of lysine and hydroxylysine as well as the guanidyl group of the arginine residue—are made nonreactive. Since the removal of the ε-amino group by diazotization evidently affects the chrome fixation only slightly, it appears that the arginine residue of collagen is the main binding center for the thiocyanatochromiate.

The sulfur values show that the compounds fixed by collagen contain on the average only *two* CNS groups per atom of Cr. Thus, other groups, probably water molecules, subsequently forming OH groups by protolysis, have entered into the chromium complex. The affinity of these chromiates for collagen is probably due to such constitutional alterations.

Stiasny and Lochmann (6) found that 1 g. portions of hide powder, treated with 60 ml. of aqueous solution of Reinecke salt, containing 100 mg. Cr, fixed only 0.44% Cr, on the weight of the dry substance, in 4 hr. The treated hide powder showed a "W.B." figure of 43. The "W.B." ("Wasserbeständigkeit") i.e., the degree of resistance to hot water, was determined by treating portions of the specimens equal to 0.5 g. of collagen in 100 ml. of boiling water for 10 hr. The amount of collagen not solubilized by the boiling water, expressed as percent of the original amount of collagen, gives the "W.B." figure. Their findings are not in conflict with the data of the present paper as evident from the corresponding figure in Table II. With their very brief period of tanning in relatively dilute solution, the chrome fixation was probably mainly in the form of the intact Reinecke salt. Only by prolonged duration of the treatment, particularly by applying stronger solutions, does a more extensive fixation occur as a result of the secondary formation of modified thiocyanatochromiates with cross-linking potency.

Table III contains some additional data from another series with hide powder and variously modified specimens of hide powder. Portions of 1.0 g. of collagen were shaken with 25.0 ml. portions of the 2.0% aqueous solution of the Reinecke salt (pH 4.8) for 3 weeks.

In Table IV the corresponding runs with calfskin pelt in solutions of pH 5.5 for 3 weeks are recorded.

TABLE III

FIXATION OF REINECKE SALT BY HIDE POWDER AND MODIFIED HIDE POWDERS

No.	Substrate	% on Dry Substance			% Cr Fixed by Collagen	Ratio of CNS:Cr in Fixed Cr Compound
		Cr	S	Collagen		
1.	Hide powder (H.P.)	3.1	3.9	80	3.9	2.0 : 1.0
2.	Heat-denatured H.P.	3.5	4.4	78	4.5	2.0 : 1.0
3.	Deaminated H.P.	2.4	–	86*	2.8	–
4.	Methylated H.P.	3.6	–	77*	4.7	–
5.	H.P. pretreated in 0.3 *M* $NaIO_4$ solution (pH 5.0) at 20° C. for 7 days	2.7	–	83*	3.3	–
6.	Wattle-tanned H.P. (64 g. fixed tannin per 100 g. collagen)	0.7	–	58*	1.2	–

*Indirectly obtained.

TABLE IV

FIXATION OF REINECKE SALT BY CALFSKIN PELT AND SPECIMENS OF MODIFIED PELT

No.	Substrate	% on Dry Substance		% Cr Fixed by Collagen	ΔTs of Washed Stock
		Cr	Collagen		
1.	Calfskin pelt	1.7	89*	1.9	+25
2.	O-acetylated pelt	1.8	88*	2.0	+35
3.	Deaminated pelt	1.0	93*	1.1	+26
4.	Pelt pretreated in 0.5 *M* $NaIO_4$ solution (pH 4.0) at 20° C. for 7 days	1.4	91*	1.5	—
5.	Codskin pelt	2.3	85*	2.7	+26

*Indirectly obtained.

TABLE V

TANNING OF PELT WITH 10.0% METHANOL SOLUTION OF REINECKE SALT

No.	State of Tanned Stock	% on Dry Substance		% Cr Fixed by Collagen	Increase in Shrink Temperature	
		Cr	Collagen		"Shocking" Method	Ordinary Method
1.	Directly from the tan bath; pressed	2.2	86*	2.6	+12°C.	+12°C.
2.	Stock pressed and freed from unfixed Cr by extraction with methanol	1.4	91*	1.5	+24°C.	+24°C.

*Indirectly obtained.

In Tables V and VI data are given for a 48-hr. tannage with Reinecke salt dissolved in methanol, in 5.0 and 10.0% solution, employing acetone- and methanol-dehydrated hide powder and calfskin pelt.

TABLE VI

FIXATION OF REINECKE SALT BY VARIOUS HIDE POWDER SPECIMENS

(From 5.0% methanol solution; 7 days)

No.	Substrate	% on Dry Substance		% Cr Fixed by Collagen
		Cr	Collagen	
1.	Hide powder (H.P.)	3.4	78*	4.4
2.	Deaminated H.P.	2.4	85*	2.8
3.	N-acetylated H.P.	3.6	77*	4.7
4.	N- and O-acetylated H. P.	2.9	81*	3.6
5.	Pretreated in 0.3 *M* solution of $NaIO_4$ at 20°C. for 7 days	2.9	81*	3.6
6.	Pretreated in water of 68°C. for 2 hr.	2.5	84*	3.0
7.	Ionic groups of collagen completely inactivated by irreversibly fixed Novolak–sulfonic acid	0.3	65*	0.4
8.	Ionic groups of collagen completely inactivated by irreversibly fixed α-fraction of lignosulfonic acid	0.4	60*	0.7

*Indirectly obtained.

A complete record of the analysis of a tanned specimen of acetone-methanol-dehydrated hide powder which had been treated in 7.5% methanol solution of the Reinecke salt for 7 days is recorded to illustrate the general procedure. The chromed stock, freed from soluble chromium compounds by methanol extraction, was dried and analyzed. On the dry weight it contained 6.0% ash, 3.9% Cr, 5.0% total S, and 4.8% nonprotein S. The total N expressed as collagen (N × 5.56) was 98.4%. The figures of Cr and nonprotein S, 3.9 and 4.8% respectively, give a ratio of CNS to Cr of 2.0 : 1.0. Thus, the chromium complexes fixed, corresponding to $[Cr(CNS)_2 \cdot 2\ NH_3]$, contained 4.2% of N, figured on dry substance, equivalent to 23.4% of collagen. Thus, the true collagen content is 98.4 – 23.4, or 75%. Accordingly, the chromium content as % Cr, based on collagen, was 5.2.

The degree of resistance of various "collagen compounds", such as those with vegetable tannins, dyestuffs, and noncationic chromium complexes, to hydrogen-bond-breaking agents, applied in the form of aqueous solutions of 8*M* urea at 20°C., has been found useful for characterization of the type of binding between collagen and the agent fixed. Formaldehyde-tanned hide powder, which is inert towards the concentrated solution of urea employed, was tanned in 2.0% aqueous solution of the Reinecke salt by the procedure

used for the series reported in Table I. The chromed specimens contained 1.0% Cr, on the weight of collagen, irreversibly fixed. By treating the chromed stock with 8*M* urea solution about one-third of the total irreversibly fixed chromium was solubilized. This finding indicates that some type of hydrogen bonding of the chromium complexes to the collagen is a part of the reaction.

DISCUSSION

The attachment of the intact $Cr(CNS)_6$ anion to collagen, both in aqueous and alcoholic systems, has earlier been found (7) to result in labilization of the protein. By secondary alterations, for instance by washing, CNS groups are displaced from the complex, and new coordination sites on the Cr atom are created, effecting stabilization (tanning) of the hide protein. The data for the present system, $[Cr(CNS)_4(NH_3)_2]$-complexes—Collagen, show that in aqueous as well as in methanol solution the Reinecke salt is *not* taken up by collagen *intact*. It is indicated by the data that a complex containing only *two* of the four original CNS groups is present in combination with the collagen. The tanning effect is definitely proven by the marked increase in shrinkage temperature obtained by the ordinary method of measuring the shrinkage temperature of leather as well as by the "shocking" technique, which is a measure of the *in situ* tannage. Further, the leather-like drying-out of the chromed collagen and its general characteristics are additional evidence that tannage has occurred. In the following, the name "Reinecke salt" is used for all the various chromium compounds present in the solutions, both the true Reinecke salt and the secondary products.

The Reinecke salt was primarily intended to be used as a reagent for measuring the altered reactivity of the hydroxyproline residue of collagen after modification of its hydroxy group, by acetylation mainly, as already mentioned. However, the non-specificity of the Reinecke salt for the prolines made it less useful for that purpose. The main reason for this non-specificity is probably its preferential affinity for the arginine residues of collagen.

From the data on the effect of modifying various functional groups of collagen upon its irreversible fixation of the thiocyanato compound, information as to the type of reaction and the functional groups involved in the binding of the chromium complexes is obtained. By esterification (methylation) of the carboxyl groups of collagen, these are made nonreactive toward ordinary cationic chromium complexes (10). In the present instance their inactivation does not impair the reaction; rather, a definite increase in chrome uptake is found, probably due to the freeing of basic protein groups (arginine groups) during the esterification. Thus, the carboxyl groups do not enter as such in the reaction as ionogenic centers. By the N-acetylation of collagen the ϵ-amino groups are blocked. The effect of this treatment on the chrome uptake is slight. On the other hand, by exhaustive acetylation of collagen with all ϵ-amino groups and the majority of hydroxy groups transformed into acetyl

compounds, some blocking of the chrome fixation results. However, in some instances the effect is hardly noticeable. Accordingly, the hydroxy groups of collagen may play a secondary role as binding centers of the protolysis products of the thiocyanatochromiates. Deamination, i.e., removal of ε-amino groups of the lysine residues, leads to diminished fixation of chromium, indicating some participation of these basic groups as loci for the chrome fixation. Heat-denaturation, as well as periodate-pretreatment of collagen, does not radically affect the reactivity of collagen. This might be construed as indicating that hydrogen bonding of the chromium complexes to the keto-imide and the hydroxy groups of collagen is not the governing reaction. However, the removal of irreversibly fixed chromium complexes by 8*M* urea solution indicates the participation of weaker valency forces of the type of hydrogen bonds (formation of molecular compounds).

By increasing the number of guanidyl groups of collagen the fixation of the chromiate is augmented. This indicates that the arginine residue of collagen supplies loci for binding of the Reinecke salt. This view receives further support by the data on the chrome fixation by the specimens of collagen, which are devoid of acid-binding groups as a result of the complete inactivation of the lysine and arginine residues. Since the ε-amino group has comparatively little influence on the reaction as shown by the data for the chrome fixation of deaminated and N-acetylated collagen, the almost complete elimination of the binding capacity of collagen for the Reinecke salt exhibited by the specimens with their basic groups completely inactivated, particularly by irreversibly fixed condensed naphthalene sulfonic acid as well as by Novolak-sulfonic acid and α-lignosulfonic acid, suggests that the guanidyl residue is the principal site involved in this type of chrome fixation.

The marked *in situ* tanning action of the secondarily formed compounds of the Reinecke salt applied to collagen in aqueous as well as alcoholic media is an interesting example of the noncationic type of chrome tannage not involving the carboxyl ions of collagen. The formation of stable complex compounds between these secondary thiocyanatochromiates and the guanidyl groups of collagen, the chromium complexes reacting multifunctionally, is indicated by the data presented to be the basis for the tanning effect. The Reinecke salt has by itself *no tanning effect*, as already shown by Stiasny and Lochmann (6).

SUMMARY

The Reinecke salt, $[Cr(CNS)_4(NH_3)_2]\ NH_4 \cdot H_2O$, possesses marked affinity for collagen in aqueous as well as in methanol solution. The complexes that combine with collagen irreversibly, which are indicated to be responsible for tanning effect, are *secondarily* formed. They contain on the average *two* CNS groups per atom of chromium. By their incorporation with the collagen, its shrinkage temperature is markedly elevated by 20°–25°C. The carboxyl

groups of collagen are not involved in the reaction. The main reactive site appears to be the guanidyl group of collagen. The protolysis products of the Reinecke salt form an interesting example of noncationic chrome-tanning agents.

ACKNOWLEDGMENT

The author is obliged to *Statens Tekniska Forskningsråd* for a grant. He is also indebted to Miss Marianne Pählman for her diligent assistance in part of the experimental work.

REFERENCES

1. Bergmann, M., and S. W. Fox. *J. Biol. Chem.*, **109**, 317 (1935).
2. Werner, A. *Ann. Chem.*, **406**, 261 (1914). *See also* Pfeiffer, P. "Organische Molekülverbindungen" (Stuttgart: Enke, 2nd ed., 1927) p. 136.
3. Kapfhammer, J., and R. Eck. *Z. physiol. Chem.*, **170**, 294 (1927).
4. Bergmann, M. *J. Biol. Chem.*, **110**, 471 (1935).
5. Gustavson, K. H. *Acta Chem. Scand.*, **8**, 1298 (1954); *Nature*, **175**, 70 (1955).
6. Stiasny, E., and C. Lochmann. *Collegium*, **1925**, 190.
7. Gustavson, K. H. *Svensk Kem. Tidskr.*, **62**, 165 (1950).
8. Thomas, A. W., and S. B. Foster. *J. Am. Chem. Soc.*, **48**, 489 (1926). *See also* Gustavson, K. H. *Svensk Kem. Tidskr.*, **52**, 261 (1940); *Kolloid Z.*, **103**, 43 (1943).
9. Green, R. W., K. P. Ang, and L. C. Lam. *Biochem. J.*, **54**, 1181 (1953). Green, R. W., *ibid.*, **54**, 187 (1953). *See also* Gustavson, K. H. *Acta Chem. Scand.*, **8**, 1299 (1954); **9**, 1049 (1955).
10. Fraenkel-Conrat, H., and H. S. Olcott. *J. Biol. Chem.*, **161**, 259 (1945). *See also* Gustavson, K. H. *J. Am. Chem. Soc.*, **74**, 4608 (1952); *Acta Chem. Scand.*, **6**, 1443 (1952).
11. Hughes, W. L., Jr., H. A. Saroff, and A. L. Carney. *J. Am. Chem. Soc.*, **71**, 2476 (1949). *See also* Putnam, F. W. "Chemical Modification of Proteins" in *The Proteins*, ed. Neurath, H., and K. Bailey (New York: Academic Press, 1953) Vol. IB, 948–49.
12. Gustavson, K. H. *Ingeniörs Vetenskaps Akademiens Handl.*, No. 177, 1944. *See also* Gustavson, K. H., and J. Tomlinson. *J. Soc. Leather Trades' Chem.*, **32**, 165 (1948).
13. ——— and A. Larson. *Svensk Papperstidn.*, **50**, 101 (1947); "Hägglunds Festskrift". Stockholm, 1947.
14. ———. *JALCA*, **47**, 151 (1952).
15. Rao, P. H. *JALCA*, **49**, 755 (1954); *see also* ref. 12 for original method.
16. Gustavson, K. H. *J. Soc. Leather Trades' Chem.*, **34**, 259 (1950); *JALCA*, **45**, 536 (1950); *The Chemistry of Tanning Processes* (New York: Academic Press, 1956) p. 70
17. ——— and B. Holm. *JALCA*, **47**, 700 (1952). Gustavson, K. H. *J. Polymer Sci.*, **12**, 317 (1954).
18. ———. *J. Soc. Leather Trades' Chem.*, **36**, 182 (1952).

Received December 9, 1957.

DETERMINATION OF N-TERMINAL AMINO ACIDS OF COLLAGEN BY THE 2, 4-DINITRO-FLUOROBENZENE METHOD

C. DEASY*

Tanners' Council Laboratory
University of Cincinnati
Cincinnati, Ohio

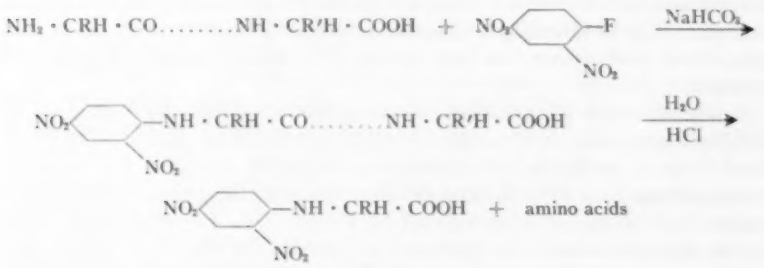
ABSTRACT

Serine, aspartic acid, and glycine were found by a modified 2,4-dinitrofluorobenzene method to be N-terminal amino acids of steerhide collagen.

—x—x—

INTRODUCTION

The 2,4-dinitrofluorobenzene method is one of the standard methods for the identification in a protein of the N-terminal amino acid (i.e., the amino acid which has the free amino group at the end of the chain) (24). This method is based on the tagging of the N-terminal amino acid by reaction with 2,4-dinitrofluorobenzene; when the tagged protein is hydrolyzed, the original N-terminal amino acid is released as a yellow dinitrophenyl (DNP) – amino acid which can be identified by a number of methods.



If the protein molecule consists of more than 1 chain, each chain contributes a DNP-amino acid.

Previous investigators (3,6) who used this method could not detect any N-terminal amino acids in collagen. At the time a number of possibilities

*Ernest Griess Fellow

were advanced to explain this result. The collagen molecule might be cyclic and therefore lack all terminal amino acids; it might be internally cyclized at the N-terminal end of the chain; or the N-terminal amino acid might be masked (for example, by a carbohydrate moiety) or inaccessible to the reagent because of steric effects.

A completely cyclic structure for collagen is now ruled out, since recent calculations from physical data from a number of different laboratories (1,4,17,19) have made it seem certain that collagen consists of a triple helix of polypeptide chains twisted around one another. Chemical evidence in support of this type of chain structure came from the determination that the collagen molecule possesses 3 C-terminal amino acids (5). Therefore it seemed worthwhile to reinvestigate the question of the presence of N-terminal amino acids in collagen.

The procedure previously used was modified in two ways which seemed likely to increase the chances of success in detecting any N-terminal amino acids.

First, the scale of the experiment was greatly increased above that previously used (3,6). The molecular weight of the fibrous collagen of skin is not definitely established, but it is certainly high compared with that of most other proteins, and therefore the relative amount of N-terminal amino acids is smaller. If, for example, the collagen molecule is assumed to be a three-chain helix of molecular weight 300,000 (8), then only approximately 0.1% of the weight of collagen consists of N-terminal amino acids (1 mg. per g.); for insulin, an example of a protein of lower molecular weight, the similar figure is 4% (40 mg. per g.). Furthermore, the yield of DNP-collagen to be expected from the dinitrophenylation of collagen is lower than that expected when soluble proteins are dinitrophenylated, because both collagen and the reagent are insoluble in the aqueous sodium bicarbonate used as the condensing medium. The DNP-collagen preparation which is hydrolyzed in the second step of the method therefore may contain an unknown amount of unreacted collagen.

A second modification was the use of milder conditions for hydrolysis of DNP-collagen, since increasing evidence is accumulating that the DNP—N bond is not so stable to hydrolysis as was originally thought. For example, yields of from 0 to 20% of some DNP-amino acids have been reported as a result of 2 to 24 hr. refluxing with 6*N* HCl (14,15,23). Therefore, short-term hydrolyses with dilute acid were used to increase the possibility of detecting any N-terminal DNP-amino acids of collagen.

EXPERIMENTAL METHODS

Collagen preparations.—Two collagen preparations were used: (*a*) steerhide corium squares (3 mm. x 3 mm.) prepared by a modification of the method of Tancous (11) in which all extractions with organic solvents

were carried out at room temperature instead of at higher temperatures, and (*b*) steerhide corium collagen (ground in a Wiley mill) prepared in this laboratory by Highberger (10). These preparations had been previously used in the determination of the C-terminal amino acids of collagen (5).

Experimental procedure.—A mixture of 25 g. steerhide corium squares (3 mm. x 3 mm.), 10 g. 2,4-dinitrofluorobenzene, and 250 ml. saturated aqueous sodium bicarbonate solution was kept in the refrigerator (5°C.) for 5 days with occasional shaking. The yellow DNP-collagen squares were then washed thoroughly with water until all excess 2,4-dinitrofluorobenzene appeared to be removed. After 3 washings with 150-ml. portions of 95% ethyl alcohol and 1 washing with 100 ml. of diethyl ether, the squares were air-dried. They were then hydrolyzed by refluxing for 4 hr. with 125 ml. of 2*N* HCl. After the hydrolyzate was cooled, it was extracted with successive 50-ml. portions of diethyl ether until the extracts were no longer yellow. The combined ether extracts were evaporated at room temperature, and the residue of yellow DNP-compounds was weighed. Twenty ml. of concentrated HCl was then added to the aqueous phase, and the solution was refluxed again for 4 hr. The second hydrolyzate was worked up exactly as the first.

A similar procedure was followed with the Highberger collagen preparation; however, since the dinitrophenylation might be expected to be more complete with this preparation, only 10 g. of the collagen was used, and the other reagents were reduced proportionately in amount.

Identification of the DNP-amino acids.—The identification of the DNP-amino acids obtained in the ether extracts of the hydrolyzates was complicated by the presence of large amounts of two other DNP-compounds, 2,4-dinitrophenol and 2,4-dinitroaniline. These compounds presumably are formed by the decomposition of the DNP-amino acids (21) and possibly also by other unknown reactions (22).

In preliminary small-scale experiments paper chromatography and ultraviolet absorption curves were investigated as methods for the identification of any DNP-amino acids present in the mixture. Paper chromatography by a number of methods (2,12,13,16,20) showed the presence of DNP-compounds other than dinitrophenol and dinitroaniline, but lack of reproducibility in the chromatography made it impossible to draw any definite conclusions. The ultraviolet absorption curves of the mixtures of DNP-compounds in the ether extracts were determined on a Beckman DU quartz spectrophotometer, since a few DNP-amino acids have characteristic absorption maxima (18). Although the mixtures necessarily gave complex absorption curves, the presence of one absorption maximum at 325 to 330 mμ indicated that DNP-glycine was probably one of the components.

In view of these difficulties in identification of the components of the mixture, the Green and Kay method (7) of column chromatography on silicic

acid–Celite (2:1) with various mixtures of organic solvents as developers was investigated for the full-scale experiments. This method provides a complete qualitative scheme for the separation and identification of 16 DNP-amino acids and 2,4-dinitroaniline. Four amino acids found in collagen—arginine, histidine, hydroxyproline, and hydroxylysine—are not included, and therefore this study cannot reveal anything about their presence or absence as N-terminal amino acids of collagen.

In the Green and Kay analytical scheme, the 16 DNP-amino acids and 2,4-dinitroaniline are separated on a column into 4 bands by means of 2 different solvent mixtures. After each band is eluted, the individual members of the group are identified by further separations on silicic acid–Celite columns with other solvent mixtures. 2,4-dinitrophenol is easily separated from the other DNP-compounds on the original column, since it is much less strongly adsorbed than any of the other compounds.

The method was used with 3 modifications. Celite Analytical Filter-Aid (Johns-Manville) was used in place of Celite 545; *n*-hexane (B.P. 69°C.) was substituted for Skellysolve B ligroin (B.P. 60°–70°C.); and elutions from the columns were made with glacial acetic acid instead of with a diethyl ether–ethyl alcohol mixture.

The Green and Kay method was excellent for the separation and identification of DNP-amino acids. Although chromatography under our conditions did not always reproduce quantitatively the original values of Green and Kay for the positions of the DNP-amino acids on the columns, the order of the amino acids on the columns was never reversed. Occasionally also the position of a single DNP-amino acid on a column might vary if 2 chromatograms were run several weeks apart; this type of behavior was reported by the original authors. Therefore, it was frequently necessary to run unknown and known samples under completely parallel conditions in the final checking. On one occasion DNP-glycine was found in Group III (instead of in its normal position in Group II), but its identification in the subsequent separations was satisfactory.

RESULTS AND DISCUSSION

From 25 g. steerhide corium squares, a total of 37.9 mg. of DNP-compounds was obtained (21.2 and 16.7 mg. from the first and second hydrolyzates respectively). A total of 18.0 mg. of DNP-compounds was obtained from 10 g. of the Highberger collagen preparation (15.3 and 2.7 mg. from the first and second hydrolyzates respectively). These amounts are of the expected order of magnitude of the N-terminal amino acids if collagen has a triple chain structure and a reasonable molecular weight is assumed. For example, they represent a yield of 58% and 69% for the corium squares and the Highberger preparation respectively, if collagen is assumed to be a triple helix with a molecular weight of 300,000. Of course, a large number of other factors—the

unknown amounts of DNP-collagen hydrolyzed, the possible incompleteness of the hydrolyses, the decomposition of DNP-amino acids during the hydrolyses, and the presence of 2,4-dinitrophenol and 2,4-dinitroaniline in the mixtures—render these calculations inaccurate, but they are of interest as an estimation of an order of magnitude.

When the mixtures of DNP-compounds obtained from either the corium squares or the Highberger preparation were carried through the Green and Kay analysis, three DNP-amino acids were identified: DNP-serine, DNP-aspartic acid, and DNP-glycine. Serine, aspartic acid, and glycine are, therefore, N-terminal amino acids of collagen from bovine corium.

In addition to the three DNP-amino acids the mixtures contained large amounts of 2,4-dinitroaniline (separated as Group III) and of 2,4-dinitrophenol, which is easily removed during the initial phase of the analysis. On one occasion a small amount of a yellow band which did not correspond to any of the DNP-compounds in the analytical scheme was found. This band occurred in the region of the column where some DNP-peptides and artifact zones adsorb (7); there was insufficient material, however, for further investigation.

The quantitative data on the amounts of the individual DNP-amino acids which were obtained after complete separation on the columns are not considered significant, since recoveries in the successive elutions were very low. However, from qualitative observations during the chromatography on the first column the amounts of the 3 amino acids appeared to be of the same order of magnitude.

It is interesting to compare the present findings of the N-terminal amino acids of collagen with the previously determined N-terminal amino acids of gelatin. Although the exact nature of the chemical changes which occur when collagen is converted into gelatin are not known (9), the reaction probably involves degradation of the collagen molecule. There is, therefore, a strong presumption that the N-terminal amino acids of collagen should be among the N-terminal amino acids of gelatin. Both Grassmann and Hörmann (6) and Bowes and Moss (3) report that aspartic acid and glycine are two of the five N-terminal amino acids of gelatin. These results are in agreement with our finding of these 2 amino acids as N-terminal amino acids of collagen. Grassmann and Hormann also find our third amino acid, serine, (which Bowes and Moss do not report) as one of the N-terminal amino acids of gelatin.

ACKNOWLEDGMENT

Appreciation is expressed to the staff of the Tanners' Council Laboratory for advice and counsel during the course of this work, and to the Ernest Griess Fellowship Fund which made this study possible.

REFERENCES

1. Bear, R. *Biophys. Biochem. Cytol.*, **2**, 363 (1956); *C.A.*, **50**, 15639 (1956).
2. Blackburn, S., and A. Lowther. *Biochem. J.*, **48**, 126 (1951).
3. Bowes, J., and J. Moss. *Ibid.*, **55**, 735 (1953).
4. Cowan, P., S. McGavin, and A. North. *Nature*, **176**, 1062 (1955).
5. Deasy, C. *JALCA*, **51**, 584 (1956).
6. Grassmann, W., and H. Hörmann. *Hoppe-Seyler's Z. Physiol. Chem.*, **292**, 24 (1953).
7. Green, F., and L. Kay. *Anal. Chem.*, **24**, 726 (1952).
8. Gustavson, K. *Chemistry and Reactivity of Collagen* (New York: Academic Press, 1956) p. 75.
9. ———. *Ibid.*, 283–87.
10. Highberger, J. *JALCA*, **31**, 93 (1936).
11. Jacobs, J. *JALCA*, **44**, 722 (1949).
12. Kent, P., G. Lawson, and A. Senior. *Science*, **113**, 354 (1951).
13. Levy, A. *Nature*, **174**, 126 (1954).
14. ——— and C. Li. *J. Biol. Chem.*, **213**, 487 (1955).
15. Mellon, E., A. Korn, and S. Hoover. *J. Am. Chem. Soc.*, **75**, 1675 (1953).
16. Monier, R., and L. Pénasse. *Compt. rend.*, **230**, 1176 (1950); *C.A.*, **44**, 7189 (1950).
17. Ramachandran, G. *Nature*, **177**, 710 (1956).
18. Rao, K., and H. Sober. *J. Am. Chem. Soc.*, **76**, 1328 (1954).
19. Rich, A., and F. Crick. *Nature*, **176**, 915 (1955).
20. Rovery, M., and C. Fabre. *Bull. soc. chim. biol.*, **35**, 541 (1953); *C.A.*, **48**, 781 (1954).
21. Schramm, G., and G. Braunitzer. *Z. Naturforsch.*, **8b**, 61 (1953); *C.A.*, **48**, 9914 (1954).
22. Schroeder, W., and J. LeGette. *J. Am. Chem. Soc.*, **75**, 4612 (1953).
23. ———, L. Kay, J. LeGette, L. Honnen, and F. Green. *Ibid.*, **76**, 3556 (1954).
24. Springall, H. *Structural Chemistry of Proteins* (New York: Academic Press, 1954), p. 315.

Received December 28, 1957.

Leather from Seaweeds (Algae). The plants are dried and powdered, and extracted with warm water in a heated boiler, with or without the addition of alcohol, soda, milk of lime or other salt. The solution is allowed to settle at a temperature of 120° to 140° F. When cold it congeals to a jelly, which is used for various purposes.

1. Transparent Sea-weed Leather is obtained by pouring the jelly upon a plate and allowing it to dry out, after other substances and various quantities of alcohol, according to the thickness and desired pliability, have been added.

2. Opaque Sea-weed Leather is produced in the same manner, except the adding of substances which give to it greater power of resistance and the desired opacity and color. Both varieties may also be spread upon muslin, or paper, or other substances, whereby, in the first case, a substitute for gutta-percha, parchment, etc., is obtained, and, in the latter case, one for wall paper, book covers, etc.

—*The Techno-Chemical Receipt Book*, ed. by W. T. Brannt and W. H. Wahl. Philadelphia: Henry Carey Baird & Co., 1892.

LIFE LINES

Brief Biographies of Our Contributors

DR. CLARA DEASY holds the Ernest Griess Fellowship and is Associate Professor of Basic Science in Tanning Research at the University of Cincinnati where she completed both her undergraduate and postgraduate work. She has taught at Oberlin College and Temple University Medical School, and carried out research on proteins at the University of Illinois and at California Institute of Technology. She has some thirty scientific publications to her credit.

DR. K. H. GUSTAVSON—See the August, 1957, *Journal.*

Artificial Leather for Lithographers' Rollers. The following mass, previously melted in a water-bath, is poured around a core about ½ inch less in diameter than the mould: syrup, 20 parts; glue, 20 parts; saltpetre, 3 parts; sugar, 3 parts; water, 5 parts; oil of almonds, 1 part; chrome yellow, 1 part. The mass, when cold, is taken from the mould, placed for 10 hours in a solution of 1 part of sulphate of alumina and 1 of potash in 10 of water, when it is dried in the air for 4 to 6 days.

—*The Techno-Chemical Receipt Book*, ed. by William T. Brannt and William H. Wahl. Philadelphia: Henry Carey Baird & Co., 1892.

Heels of Boots and Shoes, Buttons, etc., can be prepared from pulverized leather without the use of an agglutinant. Place thoroughly cleansed leather waste in a water-bath of about 150° F. for 1 hour, then carefully dry it in a revolving drum at about 150° F., and grind it to a fineness according to use intended. The ground material is pressed into moulds heated to about 240° to 250° F., and subjected for about 10 minutes to a pressure of not less than 800 pounds to the square yard. For boot heels the powder is left in the moulds until the exterior parts become hard, but the interior remains comparatively elastic. If substances are added which do not combine with the leather waste at the above heat, the moulds must be heated from 290° to 300° F. to make the leather semi-fluid.

—*Ibid.*

To Give Leather the Smell of Russia Leather. Extract dry birch bark with alcohol. Distil off the alcohol, pulverize the remaining resin, mix it with 3 parts of calcium hydrate, and distil. The oil passing over soon changes into a resin possessing an aromatic odor like that of Russia leather, and dissolves easily in oils and alcohol.

—*Ibid.*

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

OFFICERS

President—E. B. Thorstensen, S. B. Foot Tanning Company, Red Wing, Minnesota

President-Elect—Mieth Maeser, United Shoe Machinery Corporation, Research Division, Beverly, Massachusetts

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati 21, Ohio

Council

E. Daniel Lord, J. S. Barnet and Sons, Inc., 128 Boston Street, Lynn, Massachusetts.

Charles A. Martin, E. Hubschman and Sons, Inc., 415 North Fourth Street, Philadelphia 23, Pennsylvania.

Harold R. Miller, Jr., Organic Chemicals Department, E. I. du Pont de Nemours & Company, Inc., Wilmington 99, Delaware

C. David Wilson, Fred Rueping Leather Company, Fond du Lac, Wisconsin.

Frank Zeisig, Hiteman Leather Company, West Winfield, New York.

PAST PRESIDENTS OF THE A.L.C.A.

G. A. Kerr, W. H. Teas, H. C. Reed, J. H. Yocum, F. H. Small, H. T. Wilson, J. H. Russell, F. P. Vetch, W. K. Alsop, L. E. Levi, C. R. Oberfell, R. W. Griffith, C. C. Smoot, III, J. S. Rogers, Lloyd Balderston, J. A. Wilson, R. W. Frey, G. D. McLaughlin, Fred O'Flaherty, A. C. Orthmann, H. B. Merrill, V. J. Mlejnek, J. H. Highberger, Dean Williams, T. F. Oberlander, A. H. Winheim, R. M. Koppenhoefer, H. G. Turley, E. S. Flinn.

EMPLOYMENT

LEATHER CHEMIST: Production Manager with many years experience in tanning and currying of industrial leathers, adhesives, dressings and leather treatment. Experience in quality control and personnel management. Address V-100, c/o Secretary, American Leather Chemists Association, Cincinnati 21, Ohio.

ALCA-ASTM JOINT COMMITTEES ON LEATHER

Meeting October 17–18, 1957
Cincinnati, Ohio

The Joint Committee met on the afternoon of October 18, 1957, with 32 members present.

A motion made by Dr. Lollar that "each method shall contain a statement as to significance, precision and accuracy of the method, and shall be related to germane supporting evidence at the time it is submitted to the Committee on Nomenclature and Definitions" was passed by unanimous vote.

Dr. Kanagy reported upon the meeting of the Advisory Committee held the previous evening. The following points were brought to the attention of the Joint Committee: (1) Section 9 on Bond Strength of Belting Leather has been disbanded and the work turned over to Section 7, Mechanical Properties. (2) An election of officers will be held at the next meeting of the Joint Committee. The following have been named as Nominating Committee: Dr. R. M. Lollar, Chairman; L. Boor; G. Butz; C. W. Mann; M. M. Baldwin.

Dr. Baldwin, Chairman of the Research Subcommittee, requested that each member of the Joint Committee prepare a list of suggestions for submission to the Research Subcommittee in keeping with the outline set forth in the report of that committee. The attention of each member was called to the list in Dr. Baldwin's report and the chairman earnestly urged that each member solicit any ideas in keeping with this outline.

Questions were raised by several of the section chairmen as to the proper procedure for submission of methods through the Joint Committee. The following are the steps which should be observed by each section chairman: (1) The section must agree on the method and should submit it to letter ballot within the section. (2) The final form of the method should be submitted to Dr. Lollar, Chairman of the Committee on Nomenclature and Definitions. (3) Dr. Lollar will send the method to Mr. Boor, Chairman of the Editorial Committee. (4) Mr. Boor will send the method to the Secretary. (5) The Secretary will prepare and circulate a letter ballot to the entire membership of the Joint Committee.

The Chairman requested that all subcommittee and section chairmen make a real effort to get the present ALCA methods rewritten and submitted to letter ballot prior to the March meeting.

The next meeting of the Joint Committee will be held in New York City two full days some time during March.

The following reports were submitted by subcommittee and section chairmen:

Subcommittee I. Nomenclature and Definitions.—R. M. Lollar, Chairman.—A motion was offered to provide that all the technical methods presented by the several sections shall conform to the ASTM recommendations on methods presentation by containing a section on significance and one on precision. This was adopted by the Joint Committee and is the essence of our report. This action renders any other actions of our committee null and void, since none of the methods presented have contained such sections. I am writing to the several chairmen concerned to get them to modify their written forms of the various methods to conform to this action.

Subcommittee II. Sampling and Conditioning for Physical Testing.—C. W. Mann, Chairman.—At the meeting on October 18 the following matters were discussed: (1) The negative comments on the method of conditioning leather were reviewed. It was agreed that the method would be revised in accordance with suggestions to delete the reference to an alternate procedure and the reference to previous revisions. (2) Scope of sampling methods: It was agreed that the proposed methods would be written in detail similar to Federal Specifications. (3) Purpose of sampling methods: It was agreed that the methods would include recommended practices for production lot testing as well as for testing for research purposes. (4) Subdivision of sampling methods: It was agreed that the first sampling methods written would be for whole skins or hides and not end items. Three methods will be written: for sole leather, side leather, and smaller skins.

Subcommittee III.

Section 1. Disbanded.

Section 2. Physical Dimensions. J. Naghski, Chairman.—Since only two members were present (Leithauser and Naghski), a meeting of this subcommittee was not held.

Since the last meeting the subcommittee had approved the revised form of ALCA Method E4 "Thickness of Specimens". This proposed method has been submitted to the Committee on Nomenclature, Applicability and Definitions for their review.

Committee members are now reviewing a proposed draft of ALCA Method E3 "Thickness of Units". This will be revised in line with the decision of the Joint Committee on October 18, 1957, that ASTM Methods contain a statement of significance (or applicability) and precision.

Section 3. Tensile Properties. R. L. Young, Jr., Chairman.—Five methods were presented at the meeting for discussion and approval. Methods E11 "Buckle Tear" and E12 "Stitch Tear Strength, Single Hole" were approved but will have to be rewritten to include a significance paragraph; this is a requirement for all the methods. This paragraph will be included in all methods, then they will be submitted for approval.

Method E13 "Stitch Tear Strength, Double Hole" was accepted for the changes that were made, but other suggestions were added to clarify the method, so further work will be done on it. These suggestions were: (1) the use of an awl instead of the punch, since the awl gives the same kind of holes as the needle does in the sewing process; (2) the use of shoe thread or woven wire instead of stiff wire; and (3) this method can be used on heavy leather as well as light leathers. This would mean a change in the scope and also the type of thread or wire to be used.

Method E14 "Bursting Strength, Ball" was accepted with a few changes to be made before submitting for approval. This method can be adapted for heavy leathers as well as light leathers. The scope will have to be changed to include all leathers. The same apparatus can be used and sets of extra parts to fit the apparatus can be made to allow for the thickness of the leathers. This would not affect the applicability for use on all leathers. A concordance test is going to be run on this method to verify the use on all leathers.

Method E16 "Breaking Strength" was discussed and it was decided to rewrite it into two methods under breaking strength. The Grab Method will be written to fit the light leathers such as upholstery, garment, etc., since it is an essential test for these types. The Narrow Strip Method will be separate since there is no method covering this type of leather.

It is hoped to have at least seven methods ready for approval by the Joint Committee by the first of the year so that any negative votes can be resolved at the meeting in March.

Section 4. Measurement of Water Resistance. R. G. Ashcraft, Chairman. —The meeting on October 17 in Cincinnati was attended by 23 members. The following items were discussed:

Sole Leather: Dr. Kanagy presented a sketch of a machine which he has been using to determine the resistance to water penetration. He obtained values in the range of 87 minutes for untreated finished leather up to 530 minutes for Orinite-impregnated leather. The machine is to be loaned to other laboratories so that standard samples of various leathers may be tested and the results correlated. In addition the chairman will see that the present ALCA method for static water absorption is written up in the proper fashion and submitted to the ASTM.

Garment Leather: Dr. Chouinard reported that his group had found the Spray Test acceptable as a measure of surface repellency and agreed to write this up for submission to the committee. He reported that they felt that an absorption test of some nature was also required and that they had obtained poor correlation with various shaker tests due to mechanical differences. They are now investigating the static absorption of whole skins which seems to give good correlation so far. He also described the Accelerotor as a possible test method, but further refinements will have to be worked out.

Glove Leather: C. W. Mann reported they have obtained good correlation of the Tap Tester with the wet brick course and further work will be completed with samples of leather which have been subjected to a standard treatment.

Upper Leather: The Chairman submitted a tabulation of the test results obtained on 3 samples each of 9 different leathers submitted to 11 laboratories for test by 7 different methods. All the results were received with one exception. The water absorption values were received but not tabulated due to the fact that they were obtained only at the point of failure. Since a specimen failing at 100,000 cycles would naturally absorb more water than a specimen failing at 300 cycles, these figures were obviously unrealistic.

It was noted that a particular leather which resisted penetration to a high degree on all the flex-testing machines performed very poorly on the Tap Tester. Mr. Mann suggested that the probable explanation for this was the fact that the load applied to this particular leather was too high for this type of leather. He described another test in which various leathers were carefully cemented into the vamp area of a test shoe and these shoes worn in a polyethylene over-boot containing water. The leather mentioned above performed satisfactorily in this test.

It was apparent that the flex-testing machines were essentially in agreement in that the well-treated leathers gave good values and the poorly treated leathers gave poor values. It was pointed out that a single test area of a highly water-resistant leather will occasionally give a low value and it is practically impossible to test enough samples to apply a statistical evaluation.

In view of the above, it was moved and passed that the Maeser machine, as defined in Method E31, be modified to include automatic end-point detection as described in the ALCA *Journal* of July 1956, and its speed increased to the range of 180–200 r.p.m., and that the method, so modified, be submitted to ASTM.

Section 5. Surface Characteristics. R. Stubbings, Chairman.—A subcommittee (C. P. McKee, chairman; J. Casnocha; E. D. Compton; J. A. McGrath; T. Weaver) was appointed to write up ALCA Method E46 "Crocking" as an ASTM method. This committee will carefully consider the proposed KK-L-311a change to Method 3011—Crocking dated 8 November, 1956; as well as the range of leathers that can be adequately tested by this method.

Flex Testing (Room Temperature): Several different flex-testing methods will be reviewed by a subcommittee consisting of H. Haemisegger and R. Shaw, who will submit a proposal to the next meeting for the action necessary to be taken.

Cold Failure: In view of recent findings of the upholstery leather group it was decided that the present ALCA Method E42 "Resistance to Cracking at Low Temperature" is inadequate and should not be considered for an ASTM Method. A subcommittee (Stubbings, Compton, Battles) will make a preliminary examination as to whether the upholstery group method—Grenel test—can be applied to other types of leather and report back at the next meeting for action to be taken.

Scuff Resistance: A subcommittee (P. K. McKee, chairman; A. Chouinard; M. Battles; R. Stubbings; N. C. Benrud) will examine several available scuff-testing devices (International Shoe machine, Accelerotor, Lehigh device, Eastern Regional Laboratory device) in a preliminary way and report back at next meeting.

Lightfastness: A final large-scale multilaboratory test has been agreed upon to determine if any of the available laboratory fading devices agree with South Florida outdoor exposure tests. Tests involve 5 different fading devices used on 9 types of leather each in 3 colors, with each device being employed in 3 laboratories on duplicate samples for 4 periods of time each. These results will be compared with samples of the same leathers exposed in South Florida under glass for 4 periods (in terms of Langley units) at 6 different times during the year. All samples will be measured before and after fading by a color-measurement device. The subcommittee includes E. D. Compton, chairman; R. Shaw; J. A. Casnocha; H. Haemisegger; G. L. Leithauser; J. Orietas; C. K. Knisely; R. Stubbings; J. P. Norton.

The only other ALCA Method that comes under the jurisdiction of this committee that is not presently under direct study is E64 "Staining". In view of the other work of the committee and the recent work of the ALCA Finish Committee on other methods for this test, it was decided to table this method until the committee has completed some of its other work.

Section 6. No report.

Section 7. Mechanical Leathers. A. N. Compton, Chairman.—A special meeting of the Mechanical Leather Section did not take place. In the absence of the chairman, Arthur Hirsch read the former's report of October 4 to the members of the section. According to this the "Method to Determine Corrosion Produced by Leather in Contact with Metal" will again be sent to the Secretary for inclusion on the next Joint Committee ballot. Furthermore, the Packing Permeability Test will be drawn up and mailed out to the section members for another letter ballot.

F. L. Dennett and Charles Dudley of Dow Corning Corporation expressed their willingness to serve on the Mechanical Leather Section.

Test methods for rotary shaft seals have been considered as a new program item.

Section 8. No report.

Section 9. Disbanded.

Section 10. Miscellaneous Physical Properties. A. N. Kay, Chairman.—The section considered the various methods as follows:

Method E40 "Break or Pipe": The requirement is felt to depend on the type of leather involved. For heavy leathers (outsoles) the existing method is probably satisfactory, but there is considerable doubt in the section members' minds as to whether the test has any practical significance—soles being flexed grain out. Since only a few members were in attendance, the whole section is to be polled on this.

Pipe is of importance on insoles, and the chairman is to ask Mr. Bailey if he would try the Leather Grainometer on this type of leather. (Mr. Bailey had already reported that the Grainometer is not suitable for outsole leather and could not be modified economically.)

On upper leathers break is of importance, and the Proposed Test Method 4511 of KK-L-311 was considered. There was general acceptance in principle, but it was felt that (1) conditioning of the samples should be indicated; (2) the thickness of the sample should be reported; (3) a sketch or diagram of the apparatus should be included rather than just a photograph, since the identification of working parts is not clear from the latter (pars. 3.1.1.3 to 3.1.1.6); (4) sufficient information should be supplied so that the apparatus may be built (Mr. Bailey has since advised that the instrument is available from Leather Instruments Co., Box 56, Bush Terminal Station, Brooklyn 32, N. Y.) (5) only the number of wrinkles (par. 4.3) should be reported; any definition into Good, Fair, etc. is a matter of specification, not of method; and (6) proper collaborative work must be done to establish and confirm the reliability, etc. of the method, as required by the By-Laws. The Chairman is to supply copies of the method to the whole section for further consideration of this matter.

Method E43 "Stiffness": Mr. Bailey reported, by letter, comparison of the Pierce and Tinius Olsen machines. He found good correlation and the former appreciably faster. However, he feels the Pierce machine is more suited for garment and glove leathers, and the Tinius Olsen for stiffer leathers. No report was available on the Hopton machine, but Mr. Bailey is looking into this.

The cost of the Tinius Olsen machine is considered an obstacle to its wider use and adoption, and other possible methods were considered, expecially the resistance of a loop of leather to being closed. The section is to consider this further. Mr. Bailey and his subcommittee will look into it; Mr. Blaine will try a simple set-up with the Randall and Stickney Gauge; and Mr. Maeser will study it with his Instron machine.

Method E45 "Compressibility": Dr. Stubbings had examined Indentation and Durometer methods in the hope of finding a nondestructive test. It was generally agreed that the small areas involved rendered these tests of doubtful value, while it was not certain that compressibility was the only factor being measured. It was the general consensus, also, that the existing method was acceptable, even though the section doubts the practical value of the results.

Method E42 "Cold Crack of Leather": E. D. Compton and R. Shaw had supplied evidence confirming the earlier belief that cold crack of leather is not a significant factor. Dr. Kanagy and A. N. Compton wrote in the same vein, both feeling that stiffness at lower temperatures was probably of more value, the latter mentioning two minor cases where cold crack of leather might be important. It was the consensus that, to the best of the section's knowledge, no test of this property is required except for a few minor types of leather, where Method 7111 of KK-L-311 was probably suitable.

Mr. Young mentioned the requirement for an abrasion test in the Proposed Federal Specification KK-L-165 for Impregnated Leathers. This was discussed. It was the consensus that abrasion test methods were already available, but there was the always present certainty that such tests would be considered synonymous with wear-testing—with which there is no correlation, even on impregnated leathers.

The existing machines, and the principles required of a suitable machine, were discussed. While the section wishes to consider the matter further, it is the consensus that the problem is exceedingly complex and not likely to be resolved for some time. It is felt that this would be a suitable matter for the research committee to consider.

Subcommittee IV. Research.—M. M. Baldwin, Chairman.—Eight members and seven visitors were present at this meeting which was devoted to a review of the scope and activities of the Research Subcommittee. It was the consensus that it should (1) continue its listing of current investigations on methods, primarily for its internal use; (2) survey the needs for new test methods, improved test methods, and investigation of leather properties basic to test methods, and make recommendations to the Advisory Committee for action on these needs; (3) prepare a list from the above survey for publication in ASTM's "Challenges in Materials Research"; (4) recommend that selected items from this list be promoted for investigation in advanced undergraduate science courses in colleges and universities; and (5) act on problems assigned or authorized by the Advisory Committee.

The Research Subcommittee earnestly solicits suggestions from the entire Joint Committee in the above areas.

Subcommittee V. Editorial.—No report.

M. H. Battles
Secretary

"AMERICA'S NUMBER ONE SPEAKER" TO ADDRESS ANNUAL MEETING

DR. KENNETH McFARLAND
Convention Speaker

Dr. Kenneth McFarland will be the principal speaker at our annual banquet at Swampscott on May 27. In a survey conducted by the U. S. Chamber of Commerce Dr. McFarland was named "America's Number One Speaker". When Dr. McFarland was recently presented with an honorary degree, the citation said, in part:

"In a time when the art of communication is clouded by the trite phrase and repeated cliché, Dr. McFarland has spoken from his heart to the hearts of Americans, and they have responded to him .... He has used the spoken word to lift men with new visions of hope .... He is a leader who has gained the respect of businessmen, educators, and the leaders of the professions as well."

Dr. McFarland received his Bachelor's Degree from the State Teachers College at Pittsburg, Kansas. He has a Master's Degree from Columbia, and a Ph.D. from Stanford. He gained national prominence as a school executive through 24 years of service in that field and is sometimes described as "the teacher who has made the whole continent into a personal classroom." His achievements in vocational education were signally recognized when the McFarland Trade School, which he designed and built at Coffeville, Kansas, was named in his honor.

A businessman, farmer, stock raiser, civic and church leader, industrial advisor, personnel consultant, and public relations counsellor, Dr. McFarland has long been a student of government and economics, and his speeches frequently reflect his knowledge of those fields. He will talk to us through the courtesy of General Motors Corporation.

AL SCHILLER RETIRES

B. A. ("Al") Schiller has retired as manager of the Tanning Oils Division of Nopco Chemical Company after serving in that capacity for 25 years. He

will be retained by the company as a consultant. His successor is Clinton A. Retzsch.

"Al" joined ALCA in 1920. During the 1930's he performed a great and lasting service for the Association as chairman of what is now known as the Ways and Means Committee. When he took over this thankless job, the Association was very nearly insolvent because of curtailed income during the depression years. By insisting on a drastic reduction in administrative expense, setting up sound bookkeeping procedures, eliminating fictitious assets (including back dues of some members who had been dead for years), and conducting a vigorous one-man campaign for more advertisements and more members, he transformed recurrent annual deficits to comfortable surpluses. For this outstanding service to the Association he received the first Alsop Award in 1939.

DIRECTORY CHANGES

NEW MEMBERS

Thomas J. Barnet, 2 Birch Street, Marblehead, Massachusetts.
Philip D. Bixby, Boston Road, Groton, Massachusetts.
Theone C. Cordon, U. S. Dept. of Agriculture, EURDD, 600 East Mermaid Lane, Philadelphia 18, Pennsylvania.
Antonio N. Dajer, Apdo. Aereo 1471, Managua, Nicaragua, C. A.
Vincent T. Elkind, General Delivery, Bristol, New Hampshire.
Lothar Engelmann, Chemtan Company, Exeter, New Hampshire.
Stanley Friedland, American Cyanamid Company, 3505 N. Kimball, Chicago, Illinois.
J. Walter Giffee, American Meat Institute Foundation, 939 E. 57th Street, Chicago 37, Illinois.
Richard G. Herman, 9 Saltonstall Pkwy., Salem, Massachusetts.
Jose Manuel Irurita, Lowell Technological Institute, Box No. 192, Lowell, Massachusetts.
Alfred H. Korn, Eastern Utilization Res. and Dev. Div., USDA, Philadelphia 18, Pennsylvania.
Peter Lowenstein, 4580 Broadway, New York 40, New York.
Jerayr Manikian, 22 Gamewood Terrace, Lynn, Massachusetts.
Eugene A. Morrill, 71 Fairwood Road, Madison, New Jersey.
F. P. Russell, Ciba Company, Inc., 627 Greenwich Street, New York, New York.
Moises Tatarsky, Concepcion Beistegui No. 1712-301, Colonia Narvarte, Mexico City, Mexico.
Joseph Thiel, 984 S. Myrtle, Kankakee, Illinois.

CHANGES OF ADDRESS

Fred E. Artz, Howes Leather Company, Boyne City, Michigan.

Joseph A. Bassett, 37 Pemberton Road, Topsfield, Massachusetts.

Martin Baum, Marathon, Division of American Can Company, Research and Development Section, Rothschild, Wisconsin.

Arthur Billingham, Winslow Leather Company, Billingham, Massachusetts.

Paul E. Breer, Iroquois Oil, Color & Chemical Corporation, Edward Street (P. O. Box No. 86), Amsterdam, New York.

J. H. Buchmann, 299 West 12th Street, New York 14, New York.

James M. Cavanaugh, The Olson Importing Company, Inc., 20 Vesey Street, New York 7, New York.

A. C. Chase, 10827 W. Luther Avenue, Hales Corners, Wisconsin.

E. William Cook, Cyanamid of Great Britain Ltd., Bush House, Aldwych, London, W. C. 2, England.

John H. Davis, Marathon, Division of American Can Company, Rothschild, Wisconsin.

Caspar Drueding, The Benson Apts., Jenkintown, Pennsylvania.

M. Elston Fee, The Canada Starch Company Limited, P. O. Box 128, Montreal, Canada.

Theodore Feldman, 614 Dedham Street, Newton Centre 59, Massachusetts.

John T. Fitzpatrick, Union Carbide Chemical Company, South Charleston 3, West Virginia.

Jacques Giguere, Lignosol Chemical Limited, P. O. Box 2025, Quebec, P. Q. Canada.

H. D. Giles, Rohm and Haas Company, 29 Lowell Street, Peabody, Massachusetts.

Leon Gold, 99 Warren Street, Nutley, New Jersey.

William B. Hartnett, 7406 W. Garfield Avenue, Wauwatosa 13, Wisconsin.

Raymond Hauck, c/o Tanners Research Laboratory, University of Cincinnati, Cincinnati 21, Ohio.

John J. Heffernan, L. H. Hamel Leather Company, 117 Essex Street, Haverhill, Massachusetts.

M. E. Hewish, 840 Philmont Avenue, Trevose, Pennsylvania.

Joseph C. Kaltenbacher, Seton Leather Company, 849 Broadway, Newark 4, New Jersey.

George K. Kardos, P. O. Box 294, Beloeil Station, Que., Canada.

J. Stanley Kirk, Garden State Tanning Company, Fleetwood, Pennsylvania.

Philip J. Kraft, Jr., 67 Dunlap Street, Salem, Massachusetts.

Marden I. Lindsay, 4608 N. Wilson Drive, Milwaukee 11, Wisconsin.

Robert P. Manasse, Sawyer Tanning Company, P. O. Box 238, Napa, California.

Merton D. Minsky, 11 Anne Avenue, Brockton, Massachusetts.

Gabriel M. Oliensis, 729 Canterbury Road, Apartment C, University City 24, Missouri.
Carl O. Olson, Olson Importing Company, Inc., 20 Vesey Street, New York 7, New York.
Richard Payne, 2645 W. 121st Street, Blue Island, Illinois.
Herbert R. Prior, Prior Chemical Corporation, 420 Lexington Avenue, New York 17, New York.
William G. Quinn, R. R. No. 1, Chadds Ford, Pennsylvania.
Harold C. Sabean, 7 Beach Avenue, Salem, Massachusetts.
Louis Santorallo, 2220 Marsh Road, Wilmington 3, Delaware.
Kenneth H. Schlifske, 2420-A West Nash Street, Milwaukee 6, Wisconsin.
O. G. Schwaller, 1217 North 38th Street, Sheboygan, Wisconsin.
George F. Shepard, Herman Roser & Sons, Glastonbury, Connecticut.
Howard B. Simmons, Capitol Color & Chemical Company, 687 Hill Road, Winnetka, Illinois.
J. Herbert Stumpf, 1028 E. Lexington Blvd., Milwaukee 17, Wisconsin.
John E. Tarman, Betz Laboratories, Inc., Gillingham and Worth Streets, Philadelphia 24, Pennsylvania.
Jaime Terradas, Jaime Terradas Company S. A., Av. Libertad No. 768, Apartado Postal 172 (P. O. Box 172), Guadalajara, Jal., Mexico.
John D. Tomlinson, 2250 Brimby Road, Agincourt, Ont., Canada.
R. Hugh Trask, Arthur C. Trask Company, 327 S. LaSalle Street, Chicago 4, Illinois.
Jack H. Van Sciver, Shingle Leather Company, 1300 Walnut Street, Camden, New Jersey.
Herbert Weinstein, 2252 N. Elston Avenue, Chicago 14, Illinois.
E. H. Wolfe, General Dyestuff Corporation, Div. of General Aniline and Film Corporation, 435 Hudson Street, New York 14, New York.

RESIGNATIONS

Thomas Aldrich, Jr., Marden-Wild Corporation, 500 Columbia Street, Somerville, Massachusetts.
R. H. Bacon, R. H. Bacon & Company, 14 East Jackson Blvd., Chicago 4, Illinois.
David Balfour, Lignosol Chemicals, P. O. Box 2025, Quebec, P. Q., Canada.
F. P. Boehm, Solvay Process Division, One Gateway Center, Pittsburgh 22, Pennsylvania.
Don Carter, 310 Triangle, Dayton, Ohio.
James E. Cleland, Union Starch and Refining Company, 19th & Wabash Railroad Tracks, Granite City, Illinois.
Matthew M. Gallop, Phoenix Oil Products Corporation, 199 Pacific Street, Newark 5, New Jersey.
Andrew J. Gard, 12 Orchard Street, Wellesley, Massachusetts.

Francis K. Keirnan, 809 Winston Terrace, Charlottesville, Virginia.
E. R. Lobaugh, 6305 Twenty-Third Street, North, Arlington 5, Virginia.
Francis Person, Koppers Company, Inc., Chemical Division, Box 65, Monaca, Pennsylvania.
Peter Plambeck, Surgical Products Division, American Cyanamid Company, Danbury, Connecticut.
Stanley Sablosky, Ohio Wool Pulling Corporation, 904 Evans Street, Cincinnati 4, Ohio.
A. Howard Stuewe, 97 Butler Pkwy., Summit, New Jersey.
Ralph E. Thompson, Ansul Chemical Company, 828 N. 29th Street, Philadelphia 30, Pennsylvania.
George W. Twitchell, 177 Paradise Road, Swampscott, Massachusetts.

DEATHS

Thomas A. Faust, 107 Grand Avenue, Apt. 601, London, Ontario, Canada.
A. J. Mahoney, 117 Fifth Avenue, Gloversville, New York.

HOW NOT TO TORTURE YOUR AUDIENCE

"Let Them See What You're Talking About."

Every member who plans to present a paper at Swampscott should read, and take to heart, a brief paper by Lawrence P. Murphy, in *Chemical & Engineering News*, January 20, 1958, pages 67 to 70. The subject is the presentation of visual material—lantern slides mostly—a field wherein the need for improvement is notorious. A few of Mr. Murphy's suggestions follow.

"Has a speaker tormented you with illustrations that were insolvable puzzles? If so, you know that garbled drawings can hinder your understanding of what he is talking about. Charts and drawings need not be foggy jumbles, however, if the speaker knows how to plan them . . . . Show large material. You are designing murals for a wall, not illustrations for a book . . . . Try to make each illustration so simple that it can be understood instantly by your colleagues . . . . Be merciless in pruning out every word, line, or figure that isn't necessary . . . . Put only one idea in each illustration . . . . Sometimes you have to show a complicated diagram or table in order to indicate the relationships of various pieces of information. If you must do this, try to use the complicated illustration as a summary. Show it once in a while during the explanation, and again at the end, but when you talk about its individual parts, place these parts in separate illustrations . . . . Don't feel that you have to illustrate everything you say. Most of the visual material should be limited to those points that cannot be told by words

alone . . . . *Avoid tables of figures.* Use them only when your data can be presented in no other form, such as a graph or bar chart . . . . Illustrate your *talk*, not a journal article. There are many differences. . . . Notes are usually unnecessary, because the speaker, not the note, does the explaining. . . . Titles should be brief. . . . Be certain that the lettering is large enough so that the man in the back of the room can read it. Under ordinary conditions lettering on 8 x 10-inch copy should be at least an eighth of an inch high, and quarter inch letters are preferable. . . . Illustrations can ruin your talk as easily as they can aid it. If you plan the visual material carefully, however, it will help people understand what you're talking about. A good illustration pays off."

THOMAS A. FAUST

Thomas A. Faust, a member since 1908, passed away at his home in Fort Lauderdale, Florida, on January 22, 1958.

Tom Faust was a graduate of Gettysburg Academy and obtained his B.S. degree from Gettysburg College. He did graduate studies at the University of Pennsylvania. For a period of eight years he was a chemist for Yocum Laboratory in Newark; then for about thirty-eight years he was president of Yocum Faust, Ltd., in London, Ontario.

Tom, in the period of 1916 to 1928, was very active in A.L.C.A. work; he not only contributed to our scientific knowledge but often wrote philosophically about the Industry. In 1952 he was made a Life Member of the A.L.C.A.

Tom Faust had a host of friends in the A.L.C.A. and up to 1957 seldom missed a meeting. To his family and especially his son, J. C. Faust, now a member, we extend our sympathy.

ABSTRACTS

The Amino Acid Composition of Amphibian, Reptile, and Avian Gelatins. A. A. Leach. *Biochem J.*, **67,** 83–87 (1957).—Hydrolyzates of gelatins prepared from toad, python, and crocodile skins and from chicken leg tendon were analyzed by ion-exchange chromatographic techniques. Methods of purifying the gelatin precursors are described. Chicken leg tendon is similar in composition to mammalian collagens, but the composition of toad skin gelatin resembles certain fish gelatins more closely than gelatin from mammalian collagens, and the reverse is true for the two reptile gelatins. The increase in shrinkage temperature of the parent collagens is very approximately associated with an increase in hydroxyproline content [cf. Gustavson, *JALCA*, **51,** 676 (1956)] but the exceptions are sufficient to throw doubt on the hypothesis.
J.M.C.

Investigations on Bating. IV. The Improvement in Bating Activity of a Bate Liquor with Continuous Partial Re-Use. G. H. Green. *J. Soc. Leather Trades' Chemists*, **41,** 303–9 (1957).—The gradual improvement in bating activity which a freshly made bate liquor undergoes with continuous partial re-use seems to be due to the development of particular species of bacteria. Delimed goatskins were bated at pH 8 and 35°–40°C., and the influence of age of bate liquor on properties such as compressibility, silkiness of grain, and looseness of scud was studied. Addition of bacterial cultures to the normal bate medium indicated that bating action bore no relationship to gelatin-liquifying power of the bacteria. A number of bacteria, mainly *Bacillus* and *Micrococcus spp.* were isolated from used bate liquor and characterized. **V. The Influence of Lime Blast on Bating and Scudding.** *Ibid.*, 309–20.—The more thorough the removal of lime from skin prior to bating, the more readily is the scud loosened and the grain rendered silky during bating. The presence of lime blast due to microscopic particles of $CaCO_3$ in the skin makes scudding of delimed or bated skin more difficult. It also impedes the bating of goatskin but not of calfskin. Scudding can replace bating with calfskin and wool sheepskin but only partly with goatskin and hair sheepskin. Improvement was noted in crust leather prepared from hides bated by continuous partial re-use of a bate liquor. **VI. The Influence of Colloidal Enzyme Adsorbents.** *Ibid.*, 321–24.—Pieces of calfskin and goatskin were bated in the presence and absence of kaolin. The solution concentration of trypsin was the same, but with the kaolin an additional fourfold amount of adsorbed enzyme was present. Improvement in bating due to the presence of kaolin is attributed to release of adsorbed enzyme during the bating process. Doubt is cast on Wood's theory that enzyme may be carried into the skin in higher concentration than normal by being adsorbed on colloidal particles with a resultant improvement in bating.
J.M.C.

Structure of Elastin. G. N. Ramachandran and M. S. Santhanam. *Proc. Indian Acad. Sci.*, **45A,** 124–32 (1957); *Chem. Abstr.*, **51,** 12169*a*.

Basic Aluminum Chlorides. L. Walter-Levy and H. Breuil. *Compt. Rend.*, **244,** 2510–13 (1957); *Chem. Abstr.*, **51,** 12724*c*.

Water Solutions of Complex Combinations of Chromium Sulfate. I. D. Muzyka. *Legkaya Prom.*, **16,** No. 12, 34–37 (1956); *Chem. Abstr.*, **51,** 12730g.

Swelling of Fibrous Proteins. J. L. Morrison and J. F. Hanlan. *Nature*, **179,** 528–29 (1957); *Chem. Abstr.*, **51,** 12995*i*.

Relation of Collagen and Elastin (Morphological Studies). R. E. Tunbridge. *Experientia*, Suppl. No. **4,** 15–18 (1956); *Chem. Abstr.*, **51,** 13002*f*.

Chemical Studies on the Relation between Elastin and Collagen. D. A. Hall. *Experientia*, Suppl. No. **4,** 19–27 (1956); *Chem. Abstr.*, **51,** 13002*i*.

Studies on Leather Fungi. I. Morphology and Enzyme Activity of the Leather Fungi. Y. Inouye, Y. Iizuka, and T. Tazima. *Bull. Japan. Assoc. Leather Technol.*, **3,** 95–100 (1957) (English summary).—Sixty-four species of fungi were isolated from skins and leather materials. Of these, 35 species could be propagated on a medium containing added keratose; these consisted of 16 *Aspergillus* (including *A. niger* and *A. candidus*), 15 *Penicillium*, 1 *Citromyces*, and 3 unidentified species. These species were then tested for protease, lipase, and tannase activity. Some strains gave very powerful enzymatic action. **II. Selection of the Test Strains and the Antifungal Action of Phenolic Compounds.** Y. Inouye, C. Iizuka, and T. Tajima. *Ibid.*, 162–66.—Out of many mold strains growing on leather 10 were selected on the basis of resistance to CCl_3OH, enzyme activity, genus, and culture medium in which propagated. Spores of these strains were used to study the fungicidal potencies of the chlorophenols and 4-nitrophenol in a liquid medium. These strains were more resistant that *A.niger*. Fungicidal potency of the chlorophenols increased with the number of Cl atoms, and for compounds with the same number of Cl's, those containing a 4-Cl were most potent. Similar results were obtained with vegetable-tanned horse leather inoculated with these spores, but the amounts of fungicides required to suppress growth were about 10 times as great as in the liquid medium. Tests were also made with nitro-hydroxy-diphenyl, phenyl phenol, *sec.*- amyl phenol, and chloro-hydroxy-diphenyl; the last was as effective as CCl_3OH. H.B.M.

Studies on the Enzyme Depilation of Hides and Skins. I. Depilation Tests with Aerobic Bacteria and Selection of Effective Strains. H. Toyoda and A. Futami. *Bull. Japan Assoc. Leather Technol.*, **3,** 167–77 (1957) (English summary).—Out of 76 strains of aerobic bacteria isolated from hides, 22 strains (21 bacilli, 1 micrococcus) showed hair-loosening and proteolytic activity. Hair-loosening activity was measured by Lennox's method (*JALCA*, **41,** 91 [1946]), modified in that depilation load is expressed in g. per 10 hairs. Depilatory actions of trypsin, pancreatin, papain, and diastase were measured; trypsin showed less depilatory action than pancreatin, although its proteolytic activity was higher. Depilatory activities of culture filtrates from the active strains selected in the preliminary tests were measured, and also their

proteolytic activities toward collagen, keratin, gelatin, casein, egg albumin, and peptone. The exoproteases from the different bacteria did not hydrolyze the different proteins alike, and no parallel relationship was found between depilatory activity and proteolytic activity toward any substrate. Five strains of high depilatory potency were selected, of which one was notable for having less action on collagen than the others. This strain was most effective at pH 7.0–7.5.
H.B.M.

Basic Studies on Iron Tannage. VII. Some Consideration on the Reactions of Sorption and Bridging. I. M. Kubota. *Bull. Japan Assoc. Leather Technol.*, **3,** 155–61 (1957) (English summary).—The author believes that the tanning reaction comprises both sorption and bridging. The tanning mechanism of ferric coordination compounds was studied. The sorption of ferric cations follows both the Langmuir and the Freundlich adsorption isotherm relation, but the sorption of ferric anions, e.g., di- and tritartratoferriate, does not. There is a break in the adsorption curve at about 3–4% Fe_2O_3 adsorbed per 100 collagen. The sorption of ferric anion was considerably lower for deaminated hide powder. Assuming that the sorption is a first-order reaction, the velocity constants and activation energies were calculated. Activation energies were 3.04 and 3.22 Kcal. for ferric cation and ferric anion respectively, indicating that rate of diffusion is the factor dominating the sorption. The bridging reaction expressed as a first-order reaction, was studied from the T_s curve, and constants were calculated for di- and tritartrato- and dicitratoferriate (values not given in summary). The sorption and bridging reactions were then studied for simulataneous HCHO–ferric anion tannage. The sorption of HCHO and Fe_2O_3 was less than for either tannage separately. The HCHO, which tans more rapidly, elevated T_s so much that the effect of ferric anion on T_s could not be measured. This combined HCHO–ferric anion tannage appears to have considerable merit.
H.B.M.

Studies on the Manufacture of Chrome Tanning Agents by Electrolytic Reduction. III. Reduction of Cr^{6+} Compounds in the Presence of Zirconyl Sulfate in Aqueous Solutions and the Tanning Properties of the Reduced Solutions. T. Komuro and T. Uchidi. *Repts. Govt. Chem. Ind. Research Inst., Tokyo,* **52,** 277–80 (1957) (English summary).—Aqueous solutions of chromates are reduced electrolytically in the presence of Zircox ($3ZrOSO_4 \cdot 2Na_2SO_4 \cdot 1/3\ H_2SO_4 \cdot 6H_2O$), utilizing the acid formed by hydrolysis of the Zr compound. One mol of CrO_3 requires 2.90 moles $ZrOSO_4$, and 1 mole $Na_2Cr_2O_7$ requires 8.04 moles. These quantities of $ZrOSO_4$ liberate about 1.5 and 4.0 moles of H_2SO_4, respectively, on hydrolysis; these amounts are similar to the amounts of H_2SO_4 required for the electrolytic reduction in the absence of Zr salt. Analysis of calfskin and hide powder tanned in the reduced solution show that both Cr and Zr in the solution have a remarkable tanning power.
H.B.M.

New Physical Tests for Finished Leather. V. Pósa. *Bör- és Cipötechnika,* **6,** 12–17, 34–37 (1956); through *Hungarian Tech. Abstr.*, **9,** 89 (1957); cf. *JALCA,* **52,** 530 (1957).—With the nondestructive methods of testing

leather particularly the relationship between stress and strain, the limit of elasticity, effect of time, reversibility of the processes and the fatigue of the leather have not yet been elucidated. The effect of time can be neglected for elastic bodies but with leathers and in general with plastic substances it cannot be ignored (phenomena of relaxation). In case of leathers the reversibility of deformation is slight, however it must be taken into consideration. The concept of the modulus of elasticity in tension (E) must be modified similarly to variable velocity since the proportions of stress and strain are not constant with leathers. In analogy to variable velocity the modulus of elasticity is obtained as a differential quotient $E = \frac{d\sigma}{d\lambda}$ where σ = stress per unit cross section and λ = elongation in fractions of the initial length. Experimental determination can be effected graphically. The fatigue of leather can also be studied on the same sample. The modulus of elasticity is proportional to the tangent of the graph. A simple practical method for evaluation is given. Example. The modulus of elasticity of vegetable-tanned belting leather is 910 kg/cm² deformation being 11% by the old method at $\sigma = 1$ kg/mm². With the new method.

Deformation %	Mod. of Elasticity	Mod. of Elasticity of Fatigued Sample
0–3	550 kg/cm²	1180 kg/cm²
3–7	increasing	increasing
7–11	1400 kg/cm²	2880 kg/cm²

The relationship of the modulus of elasticity in shear (G) and E is dealt with, $G = \frac{E}{2(1+\mu)}$ where μ is Poisson's ratio, that of E and the coefficient of compression being $k = \frac{3(1-2\mu)}{E}$. These relationships are subject to modification for leather.

The Control of Some Dermestid Beetles by Biological Methods. R. Bashkaran and S. N. Sen. *Bull. Central Leather Research Inst., Madras*, **3**, 457–58 (1957).—The authors observed a Bethylid parasite attacking the larval form of *Anthrenux vorax*. The female Bethylid (bless her little heart!) stings the beetle larva and deposits eggs; her offspring in due course consume the beetle larva. H.B.M.

Manufacture of Glacé Kid by Two-Bath Chrome Tanning Method. Process No. 2. J. C. Deb. *Bull. Central Leather Research Inst., Madras*, **3**, 459–66 (1957).—Complete procedures are given. H.B.M.

Molecular Weights of Lignin Sulfonates as Influenced by Certain Acidic Conditions. V. Felicetta and J. McCarthy. *J. Am. Chem. Soc.*, **79**, 4499 (1957).—Lignin has been removed incrementally by treating hemlock wood in 5 steps with $NaHSO_3$-H_2SO_3 solutions of progressively increasing

acidity. Lignins of low molecular weight were removed first, and the lignins removed later were found generally to be of progressively increasing molecular weight. The lignin sulfonates in each increment were hydrolyzed in $NaHSO_3$-H_2SO_3 solutions, and a substantial decrease in molecular weights occurred. Generally similar results were obtained when purified non-dialyzable lignin sulfonates were hydrolyzed in acidic $NaHSO_3$-H_2SO_3 solutions and also in HCl soutions. Hydrolysis proceeds only to a limiting degree, and condensation seems to occur simultaneously but more slowly. The new end groups may be carbonyl and phenolic hydroxyl. Author's abstract

Spectro-visual Methods for Determining End Points. Application to Titration of Soluble Sulfate. H. Bovee and R. Robinson. *Anal. Chem.*, **29,** 1353 (1957).—Sulfate is titrated with barium chloride using tetrahydroxyquinone as the indicator. The end point is indicated by a change in color from green to blue when the sample is illuminated by light transmitted by Wratten filter No. 45. The phosphate, fluoride, nitrate, and chloride ions do interfere, but they may be removed through the use of ion exchange columns. H.R.W.

Cross-Linking of Collagen by Sulfur- and Nitrogen-Mustards. G. A. J. Goodlad. *Biochim. et Biophys. Acta*, **25,** 202–3 (1957).—The cross-linking of collagen as evidenced by increased shrinkage temperature was investigated by reacting standard hide powder with various reagents. With the N-mustards (di-(2 chloroethyl)methylamine-type), 2,4-dinitro fluorobenzene (FDNB), 1,3-difluoro-4,6-dinitrobenzene (DFDNB) and tri-acryl formal, 150 mg. of hide powder was suspended in 10 ml. of a phosphate buffer (pH 7.4) containing 10 millimoles of the reagent and the suspension agitated for 16 hr. at 37°C. With S-mustards (di-(2-chloroethyl)sulfide-type) hide powder was suspended in 10 ml. of distilled water and 0.1*N* NaOH added as required to maintain a pH between 6.8 and 8.2. Reaction time in this instance was 1.5 hr. All reacted collagens were washed thoroughly with phosphate buffer and then suspended in the same medium for the micro-shrink temperature measurement of Borasky and Nutting (*JALCA*, **44,** 830 [1949]). Treatment with multifunctional S-or-N-mustards, i.e., di-(2-chloroethyl) methylamine, tri-(2-chloroethyl)methylamine, and di-(2-choroethyl) sulfide, raised shrinkage temperature as much as 22° to 33°C. Corresponding monofunctional compounds had little or no effect on the shrinkage temperature. The multifunctional compounds are assumed to have cross-linked the collagen. DFDNB-reacted hide powder shrank at 97.5°C. while the tri-acryl formal product shrank at 89°C. The bonds between the various cross-linking agents and collagen were stable over a wide pH range with the exception that di-(2-chloroethyl)sulfide-reacted hide powder was partially unstable at pH 10.9. An ester-type linkage as well as other linkages are apparently present in this latter product. J.M.C.

Esterification of Protein and Amino Acid Carboxyl Groups by Mustard Gas and Related Compounds. G. A. J. Goodlad. *Biochim. et Biophys. Acta*, **24,** 645 (1957).—Hide powder was reacted with radioactive (^{35}S) di-(2-chloroethyl) sulfide (H) and thoroughly extracted with acetone

and ether. Samples were then incubated for 24 hr. at pH 7.5 and 38°C. in the presence of 1.2 *M* hydroxylamine. This treatment resulted in the loss of 56% of bound H as determined by radioactive measurements, whereas incubation in the absence of hydroxylamine liberated only 3% bound H. If incubation is carried out at pH 11.9 in the absence of hydroxylamine, 60% of bound H is liberated. This indicates the presence of an ester linkage between H and colagen. S-mustards such as benzyl 2-bromoethyl sulfide are shown to esterify the carboxyl group of glycine. J.M.C.

Kinetics and Mechanism of the Reactions between Chloroaquochromium (III) Ions and Silver Ions. P. J. Elving and B. Zemel. *J. Am. Chem. Soc.*, **79,** 5855–59 (1957).—The displacement of Cl from $[Cr(H_2O)_4Cl_2]$ by H_2O in the presence of Ag ion was studied in 3 to 6*M* $HClO_4$ in order to minimize the formation of basic ionic species and polymers. The dichloro complex is transformed first to the monochloro complex, and the latter to the hexaquo complex; the first reaction is much the more rapid. Both reactions are bimolecular, with rates depending on the concentrations of Cr and Ag. The reactions are many times as rapid in the presence of Ag as in its absence. The mechanism of the reactions is discussed. H.B.M.

Tracer Techniques in Fiber Research. H. J. White, Jr. *Anal. Chem.*, **29,** 1744–47 (1957).—A review with 29 references. While none of the work described was done with leather or collagen, some of the techniques could readily be adapted to studies of collagen fibers. H.B.M.

Accuracy of Quantitative Paper Chromatography in Amino Acid Determination Using Direct Photometry. H. R. Roberts and M. G. Kolor. *Anal. Chem.*, **29,** 1800–2 (1957).—A study has been made of the accuracy and precision of the quantitative paper chromatographic procedure developed by McFarran and Mills for determining amino acids in protein hydrolyzates. Known solutions of 20 common amino acids were prepared and analyzed. Each amino acid was assayed 9 times, the average value obtained, and the percent deviation of this average value from the known value calculated. Eleven acids gave average values which differed from the theoretical value by less than 2%, 13 less than 3%, 17 less than 5%. Only lysine, norleucine, and tyrosine had values more than 5% in excess of the true values. Statistical evaluation of precision showed that the assays can be repeated with good reproducibility. Authors' abstract.

Analysis of Aromatic Sulfonation Reaction Mixtures. W. H. Houff, D. R. Christie, and R. H. Beaumont. *Anal. Chem.*, **29,** 1866–68 (1957).—Aromatic sulfonation mixtures containing sulfuric acid and sodium sulfate were analyzed by a three-step procedure. Sulfonic acid was determined by titration with base of the regenerated sulfonic acid after precipitation of sulfate with barium hydroxide and passage of the filtrate through a cation exchange resin. Separate determination of total acidity and total sulfate permits calculation of both sulfuric acid and sodium sulfate. In an alternative method sul-

fonic acid, total acid, and total anion are determined to reveal the composition of the reaction mixture. Neither procedure is suitable for aryl sulfonates having insoluble barium salts, nor when anions other than sulfonate, sulfate, or hydroxide are present. Authors' abstract

Extraction and Flame Spectrophotometric Determination of Chromium. H. Bryan with J. Dean. *Anal. Chem.*, **29,** 1289 (1957).—Organic solvent extraction can be applied to the flame spectrophotometric determination of chromium in all types of samples. Chromium in the hexavalent state is selectively extracted with 4-methyl-2-pentanone from an aqueous solution 1*M* in HCl. The organic extract is aspirated directly into an oxyacetylene flame. This procedure circumvents interferences encountered when aspirating the bulk sample containing varying amounts of diverse elements and increases the spectral emission of the Cr 50-fold compared to an aqueous Cr solution. When the iron concentration in the aqueous phase exceeds 500 γ per ml., it accompanies chromium in the extraction but does not affect 2 Cr lines, including the most sensitive. Accurate measurements can be made on as little as 0.1 γ of Cr per ml. Authors' abstract

Combination Tannages. IV. Combination Chrome-Vegetable Tanning in a Single Bath. T. S. Ranganathan and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras,* **3,** 409–18 (1957).—This paper describes the preparation and analytical characteristics of chrome liquors made by reducing $Na_2Cr_2O_7$ with various amounts of a vegetable tannin (divi divi) in place of the more common reducing agents. The authors apparently expect that such liquors will yield leathers having properties like those of chrome-vegetable- or vegetable-chrome-retanned leathers, but no tanning experiments are described. Liquors were made by dissolving 100 g. $Na_2Cr_2O_7$ (dihydrate ?) in 400 ml. water, adding from 40 to 100 g. of divi divi powder, and adding 84 g. H_2SO_4 over a 2-hr. period. The reduction was done at about 100°C. Analyses of the resulting dark-brown liquors showed that basicity as determined by the official method declined very little (37.1 to 35.6) when divi divi was increased from 40 to 100% of the weight of dichromate but that Lehigh basicity declined from 34 to 19%. This is taken as evidence for displacement of coordinated OH by tannin or by some product derived therefrom. Acidity attributed to coordinated SO_4 decreased from 29 to 22%, and acidity attributed to coordinated organic anions increased from 3 to 16%, indicating displacement of sulfate and aquo groups by organic anions. pH value of the liquor declined from 2.85 to 2.4 as divi divi increased. Ion exchange studies with Amberlite IRA-120 and -400 showed that cationic Cr declined from 75 to 47.5% of the total Cr, anionic Cr increased from 9 to 15%, and nonionic Cr increased from 16 to 40% with increasing divi divi. Potentiometric titrations showed increasing buffering with increased divi divi. **V. Combination Tanning in Single Bath.** *Ibid.*, 445–58.—Hide powder samples (15 g.) were tanned with liquor equivalent to 7.5 g. Cr_2O_3 per 100 hide powder in a long float (at least 10:1) for 24 hr. The tanned samples were washed 3 times by suspension in 400 ml. water for 4 hr., then dried, and analyzed. As the ratio of divi divi to dichromate increased, fixation of Cr, over-all basicity, and sulfate acidity decreased, and protein-bound acid, complexly bound organic acid, and bound organic matter increased. Bound

organic matter may include organic anions fixed in the chrome complex or fixed tannin. The total varied only from 9 to 13 g. per 100 collagen. Further experiments were carried out with the liquor made with 100 parts divi divi per 100 $Na_2Cr_2O_7$. When the amount of Cr_2O_3 given per 100 hide powder was increased from 1.5 to 18 g., fixed Cr_2O_3 increased from 1.36 to 8.64 g. per 100 collagen, and fixed organic matter increased from 4.7 to 17 g. per 100 collagen. In this series pH was not controlled and dropped from 4.6 to 3.4 with increasing Cr given. In a series where pH value was varied from 2.5 to 4.5 fixation of Cr increased, and that of organic matter decreased with increasing pH. This is the behavior expected of vegetable tannin. Addition of NaCl equivalent to 10 moles per mole Cr_2O_3 decreased Cr fixation by a third but did not affect fixation of organic matter; a similar effect was noted on addition of 3 moles $Na_2C_2O_4$. All the results are consistent with the assumption that tannage took place by the simultaneous action of Cr masked with organic acids and divi divi tannin or a decomposition product thereof. **VI. Combination Chrome-Vegetable Tanning in Single Bath.** *Ibid.*, **4**, 1–11 (1957).—Pieces of pickled cowhide were tanned with the liquors previously described giving 2% Cr_2SO_3 on the pickled weight. The leathers were split into 3 layers which were analyzed for Cr_2O_3, fixed organic matter, and "over-all degree of tannage", calculated as [(% $Cr_2O_3 \times 2.73 \times 6.66$) + degree of vegetable tannage]. With increasing ratio of divi divi to dichromate in the preparation of the liquors Cr_2O_3 decreased in the grain and middle layers and increased of the liquors Cr_2O_3 decreased in the grain and middle layers and increased in the flesh layer; this last effect may reflect increase in particle size. Fixed organic matter increased with the proportion of divi divi, sharply above 70 divi divi to 100 dichromate. This ratio may represent the point at which not all the added tannin is oxidized. For low proportions of divi divi the flesh contained more fixed organic matter than the grain, but the reverse was true at higher proportions of divi divi. These trends were the opposite of those noted for Cr_2O_3 fixation, proving that organic matter was being fixed independently of Cr. Over-all degree of tannage for the whole leathers was the same for all liquors, that of the grain layer declining and that of the flesh increasing with proportion of divi divi. Dye-absorption tests with acid and basic dyes (fuchsins) on tanned hide powder showed that the percentage of acid dye absorbed from a solution containing an excess of dye was not affected by the proportion of divi divi in the liquor, although rate of penetration into intact leather was much faster when the liquor was high in divi divi. Uptake of basic dye increased with divi divi content of the liquor. Microscopic examination showed that angle of weave, fullness of fiber bundles, and thickness of leather increased with proportion of divi divi, while smoothness was unaffected, stretchiness decreased, tightness of break improved, and color became progressively browner. The leather pieces all had good resistance to tearing and to cracking.

H.B.M.

Manufacture of Picking Band Leather by the Sulfur-Chrome Combination Tanning Method. Process No. 2. S. N. Bose. *Bull. Central Leather Research Inst., Madras*, **3**, 419–22 (1957).—The recommended procedure includes treatment of pickled stock with $Na_2S_2O_3$, followed by 1-bath Cr tannage.

H.B.M.

The Manufacture of Glacé Kid Leather by One-Bath Chrome Tanning. Process No. 1. J. C. Deb. *Bull. Central Leather Research Institute, Madras,* **3,** 423–28 (1957).—A recommended process is described in detail. H.B.M.

Utilization of Sulfite Cellulose Waste Liquor as Tanning Material. VII. Sorption of Component Tannin by Wet Cationic Chrome Leather from Blended Tan Liquors. Y. Sakimoto and K. Katayama. *Japan J. Zootech. Sci.,* **28,** 121–25 (1957) (English summary); cf. *JALCA,* **52,** 292–93 (1957).—Wet Cr-tanned horse leather containing 4.7 g. Cr_2O_3 per 100 collagen, T_s 100°C., was retanned for 4 hr. with 200 ml. of 10% tannin solution for 150 g. wet leather. The liquors contained equal parts of 2 tannins, either at the natural pH of the blend or at pH about 5. Differential absorption of component tannins was estimated from determinations of gallic acid value and ethyl acetate value in the spent liquors. Chestnut tannin was absorbed preferentially from blends with wattle at pH 3.6–4.5 but not at 5; with mangrove at pH 2.9–4.5 (slight) and 5 (more); with Totanin at pH 5 but not at 2.9–4.6. Wattle was absorbed preferentially from blends with soluble quebracho, mangrove, and Totanin, both at natural and adjusted pH values. Soluble quebracho was absorbed preferentially from blends with chestnut at pH 3.5–4.5 (not at pH 5), and with mangrove at both pH values. Soluble quebracho and Totanin was absorbed equally at both pH values. H.B.M.

Raising the Water Resistance of Proteins. S. A. Pavlov and E. K. Pogosyants. *Nauchnye Trudy MTILP,* **4,** 3–31 (1954).—Acetylation of gelatin by $(CH_3CO)_2O$ lowers amino-N from 4.3 to 1.0%, while treatment with ketene lowers it to 2%. Nevertheless, treatment of gelatin films by ketene makes them more water-resistant than treatment with $(CH_3CO)_2O$. The treated films shrink in boiling water and do not dissolve. Dimethyl sulfate treatment leads to N- and O-methylation, and perhaps combination with peptide bonds, but does not increase water resistance. Increase in water resistance by cross-linking reactions, particularly with HCHO, is discussed. Previous acetylation of gelatin is stated not to influence the binding of HCHO. L.M.

Separation of Ferric Iron from Chromium as the Citrate Complex on Ion-Exchange Resin. C. Gualande. *Ann. chim.* (Rome), **47,** 693–97 (1957); *Chem. Abstr.,* **51,** 16197*c*.

The Structure of Collagen. M. L. Huggins. *Proc. Natl. Acad. Sci. U. S.,* **43,** 209–13 (1957); *Chem. Abstr.,* **51,** 16599*a*.

Waterproofing Leather with Organosilicon Compounds. IV. E. K. Maminov and M. G. Voronkov. *Zhur. Priklad. Khim.,* **30,** 974–76 (1957); *Chem. Abstr.,* **51,** 17216*g*.

Fixation of Casein Cover Paints [Finishes] in a Gaseous Atmosphere. I. Mustea. *Ind. Usoara* (Bucharest), **4,** 126–31 (1957); *Chem. Abstr.*, **51,** 17216*i*.

Symposium on Biocolloids. Macromolecular Fabrics in Biological Systems; Their Structure and Physiological Significance. F. O. Schmitt. *J. Cellular Comp. Physiol.*, **49,** Suppl. 1, 85–112 (1957). **Aspects of Macromolecular Orientation in Collagenous Tissues.** J. T. Randall. *Ibid.*, 113–27. **Crystallinity and Dimensional Changes in Fibrous Proteins (Collagen).** P. J. Flory. *Ibid.*, 175–83. *Chem. Abstr.*, **51,** 16610*e*.

The Effect of Chlorination and Subsequent Dechlorination on the Tanning Properties of Ligninsulfonates. A. G. Newcombe and H. B. Marshall. *Can. J. Technol.*, **33,** 152–60 (1955).—See *JALCA*, **51,** 327 (1956). H.B.M.

The Cross-Linking of Gelatin Using a Water-soluble Carbodiimide. J. Sheehan and J. Hlavka. *J. Am. Chem. Soc.*, **79,** 4528, (1957).—Treatment with an aqueous solution of water-soluble carbodiimide results in a very rapid gelation. The rate of disappearance of the carboxyl groups together with the loss of free-amino functions in the stored gelatin-carbodiimide mixture gives evidence that amide bond formation is taking place. Immediately after gelation the carboxyl value dropped to 25% of the original figure, and after reliquefaction only 10% of the amino and carboxyl groups remained. H.R.W.

Molecular Weights of Lignin Sulfonates during Delignification by Bisulfite–Sulfurous Acid Solution. E. Nokihara, J. Tuttle, V. Felicetta, and J. McCarthy. *J. Am. Chem. Soc.*, **79,** 4495 (1957).—The average molecular weight has been estimated of the sodium lignin sulfonates dissolved from hemlock, spruce, and maple woods into bisulfite–sulfurous acid solutions after several periods of treatment at elevated temperatures. With the gymnosperm woods it is found that lignin sulfonates of lower molecular weight are obtained first, and then as the time of treatment is extended, the average molecular weight of the dissolved lignin sulfonates increases to a maximum, decreases to a minimum, and finally begins to rise again. These changes are attributed to the effects of the following three processes which are thought to be proceeding simultaneously but at different rates: hydrolysis of hydrolyzable bonds in the lignin polymer, polycondensation of some lignin molecules with others, and diffusion of soluble lignin sulfonates from the wood tissue into solution. With maple wood the molecular weights of the dissolved lignin sulfonates obtained are about constant and strikingly smaller than those observed for the gymnosperm lignins.

Author's abstract

The Reptile Skin Trade in India. P. Pagnon. *J. Leather Technologists' Assoc. (India)*, **5,** 227–31 (1957).—The various species of lizards, snakes, and crocodiles that yield commercial skins are described. Snakeskins are shipped

alum- or bark-tanned, and lizards and crocodiles are cured with Khari salt. Overstretching of the skins and damage caused by using too little salt are unfortunately prevalent. H.B.M.

Investigations of Enzymes from Plant Kingdom. M. K. Dalal. *J. Leather Technologists' Assoc. (India)*, **5**, 269–74 (1957).—Besides papain and the latexes of madar and akanda plants previously investigated, the latex of *Pedilanthus tithy maloides* (Euphorbiaceae) showed marked proteolytic activity on gelatin, maximum at pH 6.0–7.5. H.B.M.

Leather Manufacture in India. Sanjoy Sen. *J. Leather Technologists' Assoc. (India)*, **5**, 316–34 (1957).— An address. H.B.M.

Possibilities of the Use of Mangrove in Leather Tanning. K. C. Roy Chowdhury. *J. Leather Technologists' Assoc. (India)* **5**, 335–51 (1957).—A discussion of ways of overcoming the excessive astringency and undesirable color of this abundant tanstuff by suitable blending, bleaching, etc. H.B.M.

Microscopical Study on the General Characteristics of Fiber Structure of V.T. Sole Leather Manufactured from He and She Buffalo Hide of Indian Origin. M. Banerjee and S. S. Guha. *J. Leather Technologists' Assoc. (India)*, **5**, 3520–54 (1957).—Samples of sole leather (15 from male and 11 from female buffalo hides) were assessed with regard to 11 characteristics. Seven of the female and only 3 of the male samples gave combined assessment rating of 4 or better. H.B.M.

Some Aspects of the Ultraviolet Absorption Spectrum of Chrome Liquors. D. Ramaswamy. *J. Leather Technologists' Assoc. (India)*, **4**, 52–57 (1956).—The U.V. absorbance of basic Cr sulfate (salt-free) increases continuously, though not linearly, between 300 and 225 $m\mu$ and is a linear function of Cr concentration at any wavelength. The differential absorption (DA) of basic Cr sulfate solutions was measured, using a solution treated with a 4- to 5-fold excess of H_2SO_4 as blank. DA measurements showed maxima at or near 245 $m\mu$. The magnitude of the DA increased with time after adding acid to the blank, presumably because the acid acts at once on non-olated OH groups and slowly on olated groups. The DA reaches a maximum on long aging, or on boiling and cooling the blank, and is a linear function of Cr concentration. When NaOH is added to $Cr_2(SO_4)_3$ solution, the DA increases with time, and the maximum shifts towards shorter wavelengths. DA increases, but not linearly, with basicity. DA measurements in the U.V. promise to be useful in studying aging and olation in chrome liqours. H.B.M.

Investigations on Leaf Tannins. I. The Heat Lability of Sumac Tannin. G. Vago. *Das Leder*, **8**, 110–13 (1957).—The tannin contents of various parts of Central European *Rhus cotinus* are as follows: leaves, 18–20%;

blooms, 3–16%; branch wood, 0.1–0.4%; branch bark, 3.7–5.7%; root wood, 0.5–1.0%; and root bark, 6–8%. The tannin in the leaves, bark, and wood differ, but aqueous extracts of all three have pH values of about 4.5. Leaf tannin is an intermediate product in plant growth and is therefore less stable than the tannin of wood or bark. Like Chinese tannin it is a galloyl-hexose-ester and decomposes first into glucose and gallic acid; then the latter decomposes into pyrogallol and carbon dioxide, but with production of some humin-like by-products. Paper chromatograms show close similarity between the extracts of *R. cotinus* and *R. coriaria* and also Chinese tannin. The chromatogram of *R. typhina* extract is similar to those above but has more lines. All show strong gallic acid lines and those of *coriaria* and *cotinus* also always show pyrogallol lines. On heating or long storage of the extracts, gallic acid and pyrogallol lines increase and tannin lines decrease. Sumac tannin may decompose in the following two ways: (*a*) by enzymatic decomposition under the influence of microorganisms, at temperatures up to 50°C., and (*b*) by thermal decomposition at higher temperatures, especially in the range above 60°. The former has been investigated for many years and can be prevented by preservatives, but the latter has received little attention. Enzymatic decomposition results in the formation of organic acids and a drop in pH, but thermal decomposition does not change the pH value. Studies were made of the decomposition of tannin solutions by holding them for two weeks in closed vessels at various temperatures. At 90°C., 30–50% of the tannin disappeared from extracts of all species of *Rhus* that were investigated. Thermal decomposition could not be stopped. Sterile liquors or those adjusted to pH 2 did not decompose at 40°, but at 90° decomposition was as rapid as for normal liquors. Velocity of decomposition was independent of concentration and of whether the leaves had been leached hot or cold. Slight control was obtained by adding 2% of naphthalenesulfonic acid or a syntan (Syntanol) to the third vessel of a 6-vat extraction battery. Dry sumac leaves contain 0.5–0.8% iron, and addition of Komplexon III to Sicilian sumac extract reduced thermal decomposition by about 20%. Chestnut leaf tannin behaves like sumac tannin. After 2 weeks at 90° the tannin content of a chestnut leaf extract was reduced from 10 to about 2.5%; solubles were reduced to one-half of their original value, and purity from 50 to 20. In a parallel test with chestnut wood extract the original purity of 74 was unchanged although considerable sediment formed. Powdered extracts are better for storage than liquid extracts, because even well-preserved liquid extracts show some loss of tannin after storage for 1 or 2 years. Sumac leaves themselves, if fresh and moist, are unstable to heat. If dried at too high a temperature or with air containing too much moisture (high humidity) the tannin content may drop to one-third of that in properly dried material, and with no change in appearance. Such leaf material is of no value for tanning. Properly dried leaves have been stored for 2 years with no loss in tannin content.

I.D.C.

Studies on Collagen. I. The Partial Purification, Assay, and Mode of Activation of Bacterial Collagenase. P. M. Gallop, S. Seifter, and E. Meilman. *J. Biol. Chem.*, **227**, 891–906 (1957).—The 3 methods used either singly or in combination to obtain purified preparations of collagenase from the crude enzyme, *C. histolyticum*, were: fractionation with $(NH_4)_2SO_4$, electrophoresis on starch, and adsorption on ichthyocol. Details are given of 3 methods

of assay which were developed with the use of ichthyocol as a definitive substrate either in the form of a suspension or in solution. The extent of enzyme activity is determined in the former case by measuring the amount of collagen solubilized, while in the latter, activity is measured by determining the change of viscosity with time. Results obtained with one method are readily interpretable in terms of the other two. Collagenase is activated by calcium but not magnesium ions. J.M.C.

Proteins and Their Degradation Products. XI. Distribution and Composition of a Partial Hydrolyzate of Gelatin by Means of Ion-Exchange Resins. K. Heyns and G. Wolff. *Z. Physiol. Chem.*, **297,** 206–11 (1954); *Chem. Abstr.*, **51,** 15646*g*.

Waste Disposal in the Textile, Leather, and Paper Industries. L. Klein. *Ciba Rev., No.* **121,** 3–32 (1957); *Chem. Abstr.*, **51,** 15845*c*.

The Action of *N*-Ethylmaleimide on Wool and Its Use for the Estimation of Sulfhydryl Groups. R. W. Burley and F. W. A. Horden. *Textile Research J.*, **27,** 615–22 (1957); *Chem. Abstr.*, **51,** 15958*h*.

Wool Grease. Hydrogenation of Wool Wax with Various Catalysts. T. Miyakawa, H. Shima, and H. Nomizu. *Osaka Kogyu Gijutsu Shikenjo Kiho.*, **7,** 207–14 (1956); *Chem. Abstr.*, **51,** 15973*i*.

Brine Curing of Hides in Fields of Sound and Ultrasonic Vibration Frequencies. A. Bolshakov. *Myasnaya Ind. S.S.S.R.*, **28,** No. 2, 16–18 (1957); *Chem. Abstr.*, **51,** 15980*g*.

Nomography in the Tannin Analysis. M. Boix Carreras. *Bol. Assoc. Quim. Espan. Ind. Cuero*, **18,** 159–69 (1954).—An application of the nomographic method of computation to (1) calculation of the analytic data of a tanning extract from the weights and (2) comparative study of the quality of tanning materials. A complete study of the method, giving tables of data and the different nomograms and their uses, is presented. J.B.B. and M.G.B.

Detannization with Polyamides. M. Boix Carreras. *Bol. Assoc. Quim. Espan Ind. Cuero*, **19,** 182–208 (1954).—Three methods of analysis are studied with hydrated polymers P66 (Nylon), P6 (Perlon), and B40 (interpolymer) to determine the possibility of application of the polyamides in the quantitative analysis of vegetable tanning materials. The results are compared with those obtained by the filter method, shake method, and direct detannization method, and are shown to be in general concordance. Sulfited extracts are less absorbed by the polyamides than by hide powder, and the fisetin of quebracho is absorbed by the polyamides and not by the hide powder.
J.B.B. and M.G.B.

Tests of Fractional Diffusion. A. Yague Gil and A. Torner Ochoa. *Bol. Assoc. Quim. Espan. Ind. Cuero*, **21,** 228–38 (1954).—A review on the works previously published on fractional diffusion. The authors apply the method to the determination of the Spanish tanning material "Gayuba", (*Arctostaphylos uva Ursi*). The normal extraction was done at 98°C. with three diffusions. The ratios of tannin to nontannin were 0.277, 0.327, and 0.564 in successive diffusions. At lower temperatures the nontannin extracted was higher; the ratio of tannin to nontannin becomes smaller by lowering the temperature. A full description of the method and tables of the results are given.

J.B.B. and M.G.B.

Colorimetry of Trivalent Chromium. M. Postavella. *Bol. Assoc. Quim. Espan. Ind. Cuero*, **18,** 138–47 (1954).—After a review of the different colorimetric methods for Cr determination as Cr^{VI} and as Cr^{III} the author presents a preview of his method for Cr determination as chromosulfuric acid $[Cr_2(SO_4)_6]$ H_6. Ten ml. of a filtered sample containing 4–5 g/l of Cr_2O_3 are boiled with 10 ml. of *N* H_2SO_4 cooled, and diluted to 50 ml., and the transmission is read. The compound has a maximum extinction at 5800 A, which makes the method not too sensitive. Compared with the volumetric oxidation method in 22 determinations, mean error of ± 1.54%, with a maximum of ± 3.6%, was found. Dibasic acids as oxalic, maleic, or α-hydroxy acids interfere with the formation of the compound. The author concludes that there is a positive advantage in adopting a colorimetric method for Cr determination in tanning industries.

J.B.B. and M.G.B.

Notes on Tannins. Application of Paper Chromatography. J. Boleda Vila. *Bol. Assoc. Quim. Espan. Ind. Cuero*, **18,** 148–58 (1954).—As an introduction a careful study of the paper chromatography method of analysis and its application to tanning extracts is made. The author uses Durieux 122 paper sheets, 52 x 52 cm., cut in two (52 x 26) or four (26 x 26), for the ascendent method. As solvents a mixture of ethanol–acetic acid–water (1:1:2), or, better, a mixture of butanol–acetic acid–water (4:1:5) is used. After 15 minutes exposure the chromatographs are observed in ultraviolet light at 3600 A. A 1% solution of Al_2O_3 in 50% aqueous ethanol is used for the detection of flavonic dyes, and ferric ammonium alum is used for the phenolic compounds. The chromatographs were also exposed to NH_3 vapors after they were dry. Paper chromatography is applied to study the evolution and qualitative analysis of an extract. The materials studied were: wattle, mangrove, myrobalans, sumac, pine, cork, chestnut, and quebracho. Pictures of the different chromatographs, as well as graphs of the results, are given.

J.B.B. and M.G.B.

Influence of Some Factors of Liming on the Surface Yield of Leather. A. A. Golovteeva. *Nauchnye Trudy MTILP*, **5,** 51–59 (1955).—Loss of surface area as a result of swelling in lime occurs only upon rupture of the main molecular chains of collagen, as occurs on too prolonged liming or addition of NaOH. Splitting up of fiber bundles and rupture of cross links between collagen chains do not decrease the area yield, nor does addition of Na_2S in amounts ordinarily used. The effect of NaOH produced from Na_2S is to be studied later. Addition of 1–2 g. Na_2CO_3 per liter is said to have a beneficial effect on area. . L.M.

The Present State of the Chemistry of Skin Proteins. I. S. Chernov and A. A. Golovteeva. *Nauchnye Trudy MTILP*, **6,** 3–26 (1955).—A review. The diketopiperazine theory of proteins is discussed. Various workers claim to have found that 25–30% of the total nitrogen of various collagens and collagen precursors is diketopiperazine nitrogen. The presence or absence of diketopiperazine in collagen is of considerable importance, having a bearing on the heat stability of collagen and its combination with tannin. A compound, insoluble in urea solution and in some organic solvents, containing 1 part diketopiperazine and 9 parts oak wood tannin has been reported. The aminoacid contents of collagen and procollagen have been studied. The larger differences found were: tyrosine, 1.4 and 0.0; phenylalnine, 4.2 and 2.3; histidine, 0.8 and 2.9. Collagen contained proline 15.1 and hydroxpyroline 14.0%, while procollagen contained 20% proline plus hydroxyproline. L.M.

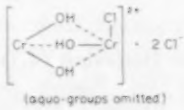
Potentiometric Study of the Rapid Formation of Basic Chromium Complexes. B. Charreton. *Compt. Rend.*, **244,** 1208–10 (1957); *Chem. Abstr.*, **51,** 11146*c*.

Anisotropic Structure in Human Elastin. A. J. Cruise. *Nature*, **179,** 674–75 (1957); *Chem. Abstr.*, **51,** 11412*e*.

Complex Nature of the Enzyme Elastase. D. A. Hall. *Arch. Biochem. Biophys.*, **67,** 366–77 (1957); *Chem. Abstr.*, **51,** 11426*c*.

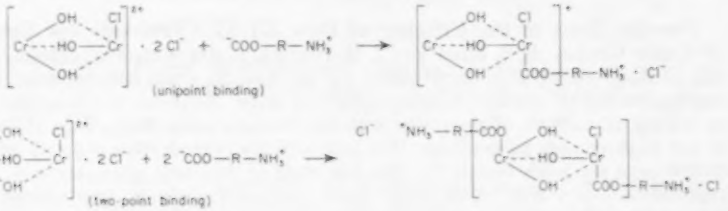
Approximation of the Proportion of Uni- and Multipoint Binding of Basic Chromium Chloride by Collagen. K. H. Gustavson. *Arkiv Kemi*, **11,** 180–94 (1957) (In English).—Only a small fraction of the carboxyls in the collagen helix are likely to be so situated that 2 of them can coordinate with a single relatively small (binuclear) Cr complex. Consequently the greater part of the cationic Cr fixed by collagen is held by a covalent coordinate link with only one carboxyl, and only a minor fraction of the Cr is bound by 2 carboxyls. The proportions of total Cr bound by one and by 2 carboxyls respectively were calculated from the proportions of Cl^- bound in different ways by hide powder tanned with $Cr_2(OH)_2Cl_4$. Hide powder thus tanned may contain 3 different forms of Cl : Cl^- bound by NH_3^+ groups (protein- bound Cl^-), Cl^- electrostatically bound by residual positive charges on Cr complexes, and Cl coordinately bound to Cr. The tanning liquor used in these experiments was shown by ion exchange measurements to be wholly cationic and to contain no coordinately bound Cl. Diffusion experiments indicated that the cationic Cr complexes contained an average of 2 Cr atoms. Finely divided, isoelectric hide powder (25 g.), previously hydrated with 50 ml. water, was tanned for 120 hr. with 250 ml. of $Cr_2(OH)_2Cl_4$ solution containing 1.2 equivalents of Cr per l. and 1 NaCl per Cr. The tanned powder was filtered by suction, washed lightly, retanned 120 hr. with 200 ml. of fresh solution containing 1 equivalent Cr per l., suction-filtered, rinsed, suspended in 1000 ml. water for 10 min., suction-filtered again, and dried. By this technique the bulk of unfixed Cr was removed with minimum alteration of the Cr complex fixed by the collagen.

The product was analyzed for Cr, collagen, total Cl, and acid Cl^- by 3 procedures. Protein-bound Cl^- was determined by titrating a sample suspended in water to equilibrium at pH 5 (see *JALCA*, **21,** 559 [1926]). Protein-bound Cl^- plus Cl^- electrostatically bound by Cr were determined by the pyridine displacement method (*JALCA*, **22,** 60 [1927]) and also by titrating a sample suspended in water to equilibrium at pH 8.2; these 2 procedures gave the same result. Cl not displaced by pyridine was considered to be coordinately bound. The results indicated that the complex Cr cation that reacted with collagen had the structure:



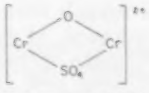
(aquo-groups omitted)

An explanation for the presence of coordinately bound Cl has been given elsewhere [see *JALCA*, **53,** 182 (1958)]. Combination of this Cr complex with collagen may occur by either of the following reactions:



If the unipoint reaction were the only one, then the tanned collagen would contain one electrostatically bound Cl^- per 2 Cr atoms while the product of the 2-point reaction would contain none at all. Actually the electrostatically bound Cl^- found by analysis was 80% of the quantity required by the unipoint reaction. From this, and from a calculation of the number of carboxyls combined with Cr at pH 3, it is deduced that about 88% of the fixed Cr is combined with only one carboxyl and only 12% with 2 carboxyls. These results agree with findings as to the combination of Cr with gelatin (*JALCA*, **48,** 559 [1953]) and of HCHO by collagen (Wiederhorn *et al.*, *JALCA*, **48,** 7 [1953]).

The Uni- and Multipoint Binding of Cationic Sulfato-Chromium Complexes by Collagen. *Ibid.*, 423–30.—The work reported above was repeated, using hide powder tanned with 33% basic Cr sulfate liquors. Two kinds of liquors were used: (1) $Cr_2(OH)_2(SO_4)_2 \cdot Na_2SO_4$ prepared by SO_2 reduction of $Na_2Cr_2O_7$, and (2) the same compound free from Na_2SO_4 prepared by reducing $CrO_3 + H_2SO_4$ with H_2O_2. Both these liquors contained cationic complexes only, consisting of 2 Cr atoms and one coordinately bound SO_4, thus:



(aquo-groups omitted)

Hide powder was tanned for 7 days with these liquors and separated from unfixed Cr under the same conditions employed in the work with chlorides. In one series hide powder was tanned 3 consecutive times for 6 hr. As the results for this product agreed closely with those for the products of 7-day tannage, it is thought that little fixation of Cr by nonionic valency forces occurred during the prolonged tannage. From determinations of protein-bound, electrostatically bound, and coordinately bound sulfate, it is deduced that 95% of the total Cr fixed was bound to only one carboxyl, and only 5% to 2 carboxyls. This multipoint bound Cr amounted to 0.7 g. per 100 collagen. H.B.M.

A New Technique for the Detection of Damaged Wool. S. K. Mitra. *Bull. Central Leather Research Inst., Madras*, **4**, 12–14 (1957).—Removal of the cuticle by bacterial action, treatment with excessive alkali, or over-chlorination is detected by dyeing with cotton blue, lactic acid, and phenol, rinsing, and examining the dyed staple under the microscope. Damaged fibers are dyed a deep blue, while undamaged fibers are white or bluish white. H.B.M.

Feedlot Tests of the Efficacy of Dow ET-57 (Trolene) for Control of Cattle Grubs. E. S. Raun and J. B. Herrick. *J. Am. Vet. Med. Assoc.*, **131**, 421 (1957).—Control of cattle grubs for the past 35 years has depended upon the application of rotenone-bearing sprays or dusts. Rotenone has been reported as killing 48 to 90% of the grubs with the average being 85%. This efficiency is not high enough to eradicate this pest with its reproductive capacity of 600 to 800 eggs per adult female fly. The life cycle of the cattle grub is given. With past control practices cattle grubs were vulnerable only in two stages: (1) while encysted in the subdermal tissues where chemicals could be applied to them, and (2) in the adult stage. Attempts to kill or repel the adult flies have been only partially successful. In 1948 a method of transplantation of the grub larvae to rabbits, goats, and mice was used during the testing of approximately 200 chemicals as chemotherapeutic agents. In 1954 and 1955 experiments with systemic insecticides for destruction of cattle grubs were reported. In 1955 screening tests at Kerrville, Texas, revealed a systemic insecticide, an organic phosphate *O,Ó*-dimethyl-*O*-2,4-5-trichlorophenyl phosphorothicate (Dow ET-57), was nearly 100% effective in controlling the grubs when it was given, at a dosage of 100 mg. per kg. of body weight, as a capsule, a bolus, or a drench. Toxicity tests at this level indicated no signs of poisoning in treated animals. Treatment preceded the normal appearance of the grub larvae by two or three months. Grubs in treated animals apparently were killed before they reached the animals' backs. An experiment was conducted in December, 1956, using 154 head of Montana and Colorado Hereford steers on full feed. Animals selected at random were placed in two pens, 77 to a pen. The animals for treatment with Dow ET-57 had an average weight of 883 lb., while the untreated animals averaged 903 lb. The treated animals were each given gelatin capsules containing Dow ET-57 at a dosage of 110 mg. per kg. of body weight. At the end of 106 days observation the animals were weighed and slaughtered. Results of the tests indicated a 95% reduction of the grubs before they reached the subcutis of the back region (49 grubs in the treated animals and 911 in the untreated animals). The treated steers each gained an average of 19 lb. more than the untreated animals. Treated animals gained 2.48 lb. per day compared

with 2.33 lb. per day for the untreated animals. Saving in feed was $3.98 a head, a total of $298.76 for the treated animals. Initially the treated animals showed severe intoxication from the treatment, going off feed for two or three days and not returning to the consumption level of the untreated steers for nearly two weeks. It is believed that the intoxication can be averted by treating animals before they are placed on full feed or by withholding water for 24 hr. prior to treatment and then allowing them to drink all they desire. J.J.

Effluent Disposal Plant. Anon. *Leather Trades Review*, **126,** 298 (1957). —The article describes a compact and efficiently designed treatment plant having a capacity of 1,000 gal. per hr. A graphic sketch diagram and photographs of various operations in handling the effluent complete the description. J.J.

Complexometric Titration of Chromium (III) Ion. R. Weiner and E. Ney. *Z. Anal. Chem.*, **157,** 105–9 (1957); *Chem. Abstr.*, **51,** 17573*c*.

Peculiarities in the Structure of Collagen. N. S. Andreeva, N. G. Esipova, and M. I. Millionova. *Kristallografiya*, **2,** 470–74 (1957); *Chem. Abstr.*, **51,** 18038*h*.

X-Ray Studies of Compounds of Biological Interest. J. C. Kendrew and M. F. Perutz. *Ann Rev. Biochem.*, **26,** 327–72 (1957); *Chem. Abstr.*, **51,** 18041*c*.

Collagen. II. Cylindrical Lattice Structure of Collagen. V. Sasisekharan and G. N. Ramachandran. *Proc. Indian Acad. Sci.*, **45A,** 363–76 (1957); *Chem. Abstr.*, **51,** 18043*h*.

Soluble Collagen from Tendon. H. Noka. *Nippon Kagaku Zasshi*, **76,** 981–83 (1955). **Molecular Size and Shape of Collagen from Rat-Tail Tendon.** *Ibid.*, **76,** 978–80; *Chem. Abstr.*, **51,** 18055*f*.

The Fermentative Loosening of the Bristle from the Derma. S. A. Kuraitis. *Legkaya Prom.*, **16,** No. 6, 24–5 (1956); *Chem. Abstr.*, **51,** 18665*j*.

The Effect of Liming on the Fine Structure of Collagen. A. L. Zaides. *Nauch. Issledovatel. Trudy Tsentral. Nauch-Issledovatel. Inst. Kozh.-Obuv. Prom.*, **1954,** No. 22, 53–61; *Chem. Abstr.*, **51,** 18668*f*.

Colorimetric Analysis with Organic Reagents. J. H. Yoe. *Anal. Chem.*, **29,** 1246 (1957).—The Fisher Award Address. This is a review of the developments over the last 35 years of instrumental and chemical aids for the qualitative and quantitative colorimetric analyses of inorganic ions. Search

and research in recent years using organic color reactions with inorganic ions have resulted in the recommended use of a number of organic colorimetric reagents. A table is given listing 16 inorganic ions that can be determined by one or more of 32 organic reagents. The wavelength of maximum absorbance is listed for most of the reagents, together with the recommended concentration range and the sensitivity of the color development. H.R.W.

Microdetermination of Volatile Aldehydes. I. R. Hunter and E. F. Potter. *Anal. Chem.*, **30,** 293–95 (1958).—In the microdetermination of volatile aldehydes, particularly those generated by and distilled from ninhydrin oxidation of amino acids, the aldehydes are absorbed in, and made to react with, an excess of $NaHSO_3$ to form stable complexes. Excess bisulfite is removed by oxidation with iodine. A measured amount of iodine in excess of the aldehyde-bisulfite equivalent and an alkaline buffer are added to the residual aldhyde-bisulfite complex. The iodine quantitatively oxidizes the bisulfite and aldehydes. Excess iodine is then determined by back-titration with standard thiosulfate. A blank is run at the same time, and the difference in titration values is used to calculate aldehyde equivalent. Authors' abstract.

Tan Fractions in Indian Vegetable Tanstuffs. S. K. Barat. *Leather Trades Review*, **126,** 362 (1957).—This is an account of preliminary investigation of goran (*Ceriops rexburghiana*), sonali (*Cassia fistula*), myrobalans (*Terminalia chebula*), and wattle tannins. These were purified and fractionated by extracting the tannins with acetone, evaporating the extract under vacuum, dissolving the concentrated extract in water, filtering off the insoluble material, and finally extracting the aqueous solution with ethyl acetate at various pH values. Evaluation of the extracts was made by determining gelatin number which is described as parts by weight of tannin fixed by 100 parts of gelatin. The results of this evaluation are given. J.J.

Effect of Acid and Salt Adjustment in E. I. Tannage with *Peltophorum Ferrugineum* Bark. M. K. Udaya Varma, E. C. Mathew and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **4,** 45–53 (1957).—Addition of Na_2SO_4, Na lactate, or HCOONa to *Peltophorum ferrugineum* tan liquors improved the color of the resulting leathers, retarded tannin penetration, and increased the plumpness and firmness of the leathers. H.B.M.

Karada Bark — A Substitute for Mimosa. J. B. Sarkar. *J. Leather Technologists' Assoc.* (India), **5,** 370–73 (1957).—In very small-scale experiments leather of satisfactory color, free from crackiness, was produced by tanning with blends of Karada (*Cleistanthus collinus*) bark and myrabalans. Blends of Karada and myrabalans with goran or babul gave unsatisfactory results. H.B.M.

Spectrophotometry in Leather Research. VIII. Investigation of Chrome Complexes with Inorganic Acids and Salts. D. Ramaswamy

and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras,* **4,** 37–44 (1957).—The differential absorption (DA) of solutions of salt-free $CrOHSO_4$ treated with inorganic acids and salts was measured. The region studied was from 230 to 300 mμ. Both the molar ratio method and Job's continuous variation method were employed. In the latter case the mixed solutions were boiled and brought to equilibrium at pH 3.0–3.2. No evidence was found for formation of complexes with Na_2SO_4, NaCl, or boric acid at the concentrations employed. Slight evidence found for complex formation with Na_2SiO_3 is of doubtful validity because of precipitation. Na_2SO_3 and KCNS gave well-marked maxima for the DA curves, at 1 Cr to 1 SO_3 or CNS. On the other hand, Calgon and KF gave minima in the DA curves, at 1 Cr to 2 F and 2 Cr to 1 Calgon. Again, these results are of doubtful significance because of precipitation. It is suggested that SO_3 and CNS may displace water molecules and F or Calgon may displace hydroxyl groups from complex combination with Cr. H.B.M.

Availability to Dinitrofluorobenzene of Some Amino Groups in Human Dentin and Ox Hide Collagen. C. C. Solomons and J. T. Irving. *Nature,* **178,** 548 (1956).—Differences in availability of the epsilon-amino groups of lysine and hydroxylysine in human dentin and ox hide collagen suggest that these groups may play a part in the combination of mineral material with the protein matrix of human dentin. R.M.L.

Elastin, A Metabolically Active Lipoprotein. F. S. Labella. *Nature,* **180,** 1360–61 (1957).—Elastin protein is a lipoprotein and more metabolically active than heretofore regarded. Unsaturated fatty acids are essential for maintaining the integrity of the fibrous protein. R.M.L.

Proteolysis of Collagen. G. H. Green. *Nature,* **180,** 93 (1957).—Collagen and procollagen are denatured by tryptic enzyme prior to hydrolysis. R.M.L.

Hydroxyproline and Thermal Stability of Collagen. D. A. Hall and R. Reed. *Nature,* **180,** 243 (1957).—Human dermal collagen specimens from 14 individuals of ages varying between 7 and 89 were studied. The hydroxyproline content varied between 12.3 and 14.3 g. per 100 g. dry collagen independent of age. Two individuals had collagen resistant to collagenase and which had a high shrinkage temperature, 72°–79°C. Two individuals had collagen which was very sensitive to collagenase and a low shrinkage temperature 60°–65°C., in contrast to normal collagens which shrank at 62°–69°C. by the micromethod used. These differences were independent of hydroxyproline content. R.M.L.

Optical Rotation and Infrared Spectra of Some Polypeptide and Protein Films. A. Elliott, W. E. Hanby, and B. R. Malcolm. *Nature,* **180,** 1340–41 (1957).—A carbonyl band is observed at about 1660 cm^{-1} in polypeptide spectra not only of the alpha helix and collagen folds but also in what seems

to be a disordered state. It must be concluded that substantially all peptide H-bands are formed in what appears to be a disordered state. R.M.L.

The Neutralization of Acid-treated Wool by Solutions of Sodium Carbonate. R. P. Harker. *J. Soc. Dyers and Colourists*, **73**, 554–60 (1957).—Neutralization of acid-treated wool by solutions of Na_2CO_3 has been examined by measuring H-ion concentrations. A qualitative interpretation of the results is given, and a quantitative treatment employing the Donnan theory of membrane equilibria has been examined, with partial success. R.M.L.

A Study of the Variables Encountered in Natural Light Fading. AATCC Committee; J. E. Norton, Chairman. *Am. Dyestuff Rep.*, **46**, 861–83 (1957).—The sun-hour method or any natural light method in which exposures are calculated or expressed on the basis of time only can not be valid or reproducible. In natural light exposures, the greatest contributing factor in the amount of color change produced is the total amount of radiation received. Langley units which integrate time and intensity of radiation in units of g. cal/cm^2/min appear to be a satisfactory measure of total radiation received. Factors also affecting color change, although to a lesser degree, are specimen temperature, moisture content, radiation intensity, and spectral distribution. R.M.L.

Two New Drycleaning Test Methods. AATCC Committee Report. *Am. Dyestuff Rep.*, **46**, 859–60 (1957).—Methods to evaluate the stability of dyed and printed fabric in terms of colorfastness and surface finish durability during drycleaning are given in the form of instruction for their use. R.M.L.

The Dyeing of Wool, Hair, and Polyamide Fibers with Metal Complex Dyes. E. Schoenpflug. *Am. Dyestuff Rep.*, **46**, 851–58 (1957).—At the present stage of their development we have 4 groups of anionic metal complex dyes: (*a*) 1:1 metal complex dyes with sulfonic acid groups: (*b*) 1:1 metal complex dyes reacted with colorless complex builders, and which contain solubilizing groups but no sulfonic acid groups; (*c*) 1:2 metal complex dyes containing solubilizing groups but no sulfonic acid groups; (*d*) 1:2 metal complex dyes without any solubilizing groups. In the 1:1 metal complex dyes there is one metallic atom for each dye molecule; the 1:2 metal complex dyes on the other hand contain one metallic atom for every two dye molecules. All types of metal complex dyes can be considered in dyeing mixtures of polamide fibers and wool, but the type of dye and dyeing method needed to give the best solid effect vary from case to case. R.M.L.

Molecular Organization in Keratins. III. The Densities of Physically and Chemically Modified Wools. R. D. B. Fraser and T. P. MacRae. *Textile Research J.*, **27**, 867–72 (1957).—A series of density determinations on physically and chemically modified wools shows that extension up to 70% and supercontraction of 15% in steam are not accompanied by density changes.

In contrast, residues from chemical extractions and enzymatic digestions show significant increases. Cortical cells fractionated from trypsin digests by gradient column techniques have densities comparable to that of porcupine quill tips. Although the density is clearly influenced by existing differences in chemical composition, estimates of relative crystallinity based on density are probably less affected by minor differences in composition than estimates obtained from meaurements of sorption and deuterium exchange. R.M.L.

The Fine Structure of Keratin. E. H. Mercer. *Textile Research J.*, **27**, 860–66 (1957).—Both the cortex and cuticle of wool are cellular, and the normal constituents of biological cells are still present in a dried and altered form along with intracellular deposits of keratin in the final fiber. The fibrous keratin of the cortical cells consists of condensed bundles or fibrils of fine filaments (alpha-filaments, width ca. 60 A.). Further, the large bundles may be extensively fused laterally to give massive irregular aggregates (0.05 to 0.2 microns). This condensation is more extensive on the para side of the wool fibrils than on the ortho (outer face of the crimp wave), and explains the greater insolubility of the paracortex. The alpha-filaments are held together in the fibrils by a cement which does not appear to be fibrous and which has a higher cystine content than the filaments. This same cement holds the fibrils together when they are fused into aggregates. The protein of the cuticle is not fibrous and appears to bear some resemblance to the cement substance of the cortex. R.M.L.

Investigation of the Molecular Weight of Sulfite Liquors. K. Barany, F. Guba, and G. Tamasovits. *A Magyar Tudomanyos Akademia Merestechnikai es Muszerugyi Intezete Kozlemenyei (Proc. Inst. Measuring Technique and Instruments Hungarian Acad. Sci.)*, **1956**, No. 1, 5–8; *Hungarian Tech. Abstr.*, **9**, 120 (1957).—According to theoretical considerations if a good tanning agent is to be obtained from sulfite waste liquor, the fractions having molecular weights of 1000 to 3500 must be removed. After dialysis the sulfite liquor was separated into 2 fractions through precipitation with alcohol. To determine the molecular weight of the fractions a method based on diffusion, pycnometric, and viscosimetric measurements was evolved. For calculating the molecular weight the following equation was obtained:

$$M = \left(\frac{RT}{6\pi MoN}\right)^3 \times \frac{4\pi N}{3} \times \frac{1}{VD(f/f_0)^3}$$

where R=gas constant, T=absolute temperature, N=Avogadro constant, N_o=viscosity of the solvent, V=partial specific volume of the solution, D=diffusion constant of the solution, and f/f_o=friction coefficient of the solution. According to the results of measurements the molecular weight of Fraction I is 6000±800 and that of Fraction II is 800±100. The first fraction constitutes 40% and the second 60% of the original material.

Experiments for Utilizing Aluminum in the Production of Tanning Agents. M. Hollo. *Kohaszati Lapok*, **11**, 475–78 (1956); *Hungarian Tech.*

Abstr., **9**, 119 (1957).—Aluminum can be employed to good advantage in certain stages of the production of tanning agents and of the tanning procedure. From among the equipment used for the above, diffusion cells and their heat exchangers, thickeners, receivers, and their joints and pipings can be made of 99.5% Al without danger of corrosion. The use of iron vessels lined with Al is advisable from the standpoint of strength for receivers and for steam-heated autoclaves.

Strength and Elasticity of Finished Leathers at Different Stresses. G. Toth and V. Posa. *Acta Tech. Acad. Sci. Hungaricae*, **16**, 291–310 (1957) (in German); *Hungarian Tech. Abstr.*, **9**, 113–14 (1957).—Various stress indexes used to characterize the quality of finished leathers were converted to an identical unit of measurement (kg/cm²). A method was elaborated for measuring pure shear stress; the stitch tear strength and tongue tear strength have been computed in kg/cm². Test conditions were chosen to obtain uniform load on the stressed cross-sectional areas. It has been found that the shear strength and resistance to rupture at sewing, stitch tear, and tongue tear stresses under identical conditions and expressed in kg/cm² are of the order of magnitude of the tensile strength. Measurement of the modulus of elasticity in compression is dealt with in detail, and a comparative tabulation is given on the correlation of the compressive bending and shear moduli of elasticity for various leathers. The various moduli of elasticity differ from one another.

Tannins and Polyphenols of *Schinopsis* (Quebracho) SPP; Their Genesis and Interrelationship. H. G. C. King and T. White. *J. Soc. Leather Trades' Chemists*, **41**, 368–83 (1957).—Laboratory extracts of the heartwood, sapwood, bark, leaves, and twigs of *Schinopsis balansae* and *S. lorentzii* were examined by two-dimensional paper chromatography and a considerable number of polyphenols identified. Most of the polyphenolic substances present in the extracts of the leaves, twigs, and bark are galloyl or quinic acid derivatives. No substances which can be regarded as "condensed" tannins can be found in the leaves or twigs, but small amounts of d-catechin are present in the bark. Galloyl derivatives formed in the leaves are passed down the plant into the sapwood, which contains significant amounts of d-catechin also. Formation of typical heartwood polyphenols which constitute quebracho tannin extract involves the loss of gallotannins of the sapwood, of the d-catechin, and two leucoanthocyanins. Consideration of the over-all results in the light of knowledge of other tannin-producing members of the *Anacardiaceae* suggests that the quebracho trees synthesize only "hydrolyzable" tannins in the leaves and that these tannins constitute the polyphenolic raw material which is ultimately converted to the typical "condensed" tannins of the heartwoods. J.M.C.

The Acid Mucopolysaccharides of Connective Tissues. II. Further Experiments on Chondroitin Sulfate. B. P. Hoffman, A. Linker and K. Meyer. *Arch Biochem. Biophys.*, **69**, 435–40 (1957).—The yield of mucopolysaccharides from top, middle, and flesh sections of bullhide was determined and compared with that of adult and embryonic pigskin. The hyaluronate yield in the top layer of the bullhide was twice that in either of the other

layers. The concentration of chondroitin sulfate B (ChS-B) varied little between layers and was almost double the concentration of hyaluronic acid in the middle and flesh layers of skin. Besides ChS-B and hyaluronate both pig and bullhide yield a small fraction of ChS-C. A fourth polysaccharide completely resistant to testicular hyaluronidase is also present. ChS-B was desulfated by treatment with methanol and HCl to yield a product completely resistant to both testicular and bacterial hyaluronidase. This is in exact contrast to ChS-A. A main constituent of ChS-B is iduronic acid. ChS-B is associated in skin with coarse-type collagen bundles and hence is absent in cornea, hyalin cartilage, and bone. Also in the top layer of skin, where collagen bundles are fine, ChS-B is low and may be absent. J.M.C.

The Effect of Freeze-Drying on the Soluble Proteins of Bovine Hide. D. R. Cooper. *J. Soc. Leather Trades' Chemists*, **41**, 387–94 (1957).—The soluble proteins present in the ground substance of hide or skin may be denatured to a greater or lesser extent depending on the method of dehydration employed during curing. The method which should cause least denaturation of the soluble proteins (i.e., freeze-drying) does affect solubility of some components. An NaCl extract of a skin taken from a freshly killed cow was examined by electrophoresis and ultracentrifuge methods. Five electrophoretic and two ultracentrifuge components were observed. The salt-soluble constituents are essentially serum proteins, other noncollagenous proteins, and mucopolysaccharides, with a very small percent of collagenous protein. Freeze-drying affects the solubility of the noncollagenous proteins other than serum proteins and by this means reduces the rehydration of hide. More drastic drying denatures serum proteins as well. Solution of the insoluble components of the freeze-dried extract with a detergent suggests that this may be a useful additive for soaking back cured stock. J.M.C.

Changes in the Mechanical Properties of Collagen Fibers during Vegetable Tannage. R. G. Mitton and F. R. Morgan. *J. Soc. Leather Trades' Chemists*, **41**, 383–87 (1957.—To study how the various tanning procedures influence fiber extensibility, the load needed to give an extension equal to 10% of the unstressed length of fibers in the raw, dry state was determined for several pretanning and tanning treatments. Single acetone-dehydrated collagen fibers were used. In the pretanning processes the extensibility changes were rapid and relatively small. Tannage in 40° Bk. wattle liquor resulted in a steady decrease in extensibility over 6 days, and further tannage with 140° Bk. liquor resulted in another steady decrease over two days. Dried tanned fibers had extensibilities comparable with raw, dry fibers. After tannage prolonged soaking in solutions of sulfated cod oil increased extensibility slightly. This result is consistent with the view that oil does not penetrate the structure of the fibrils but merely increases lubrication between them. J.M.C.

Influence of Different Methods of Beamhouse Work, Tannage, and Subsequent Treatments on the Area Yield of Chrome Upper Leather. C. A. Danon. *Commun. Fac. Sci. Univ. Anakara, Ser.B*, **8**, No. 1, 45–76 (1957).—Fourteen lots of 8 calfskins were processed, one by a standard pro-

cedure, 2 with changes in the unhairing process, 9 with changes in the tanning process, and 2 with changes in the drying process. Thickness and area were measured at 6 stages and were expressed as percentages of the values found after soaking. The finished leathers were assessed for fullness, character of flanks, feel, and general appearance. The only lots that gave a materially greater area yield than the standard (about 8–10% increase) were a lot limed with 0.4% As_2S_3 and 2% Na_2S for 3 days instead of with 3.75% Na_2S, and a lot that was wet-tacked. The latter lost 17% in thickness, but the former did not. The variations in thickness yield appear to be quite erratic; thus, 10 lots all limed alike gave thicknesses after liming that varied from 107 to 131% of the thickness after soaking, and the thickness after finishing generally conformed to the thickness after liming regardless of the method of tanning. Only 2 lots gave over-all assessments equal to or better than the standard lot; these were a lot tanned with phthalate-masked liquor and a lot tanned with Cr alum and HCHO in the same bath. Chemical analyses showed the importance of determining SiO_2 and of double precipitation of $Al(OH)_3$. All the leathers except that tanned with formate-masked liquor withstood the boil test. Dilation on heating to the boil did not seem to be related to the Cr_2O_3 content.

H.B.M.

Treatment of Tannery Waste–Sewage Mixture on Trickling Filters. B. L. Rosenthal. *Leather Mfr.*, **74,** No. 12, 20 (1957).—Described is a method of treating tannery waste in municipal sewage. The results show that tannery wastes, if pretreated with flue gas to precipitate lime, can be successfully treated on the municipal sewage trickling filter at a high rate with recirculation. With a loading of 3500–4000 pounds of B.O.D. per acre-foot per day the efficiency can be expected to be 88–89%.

J.J.

New Concepts and Work in the Field of Collagen Science. A. Mikhailov. *Tanner* (India), **12,** 209–10 (1957).—A summary, in English, of remarks of the author at the 5th Congress of the IULCS. Collagen is believed to consist of two structurally dissimilar protein complexes which were separated by extracting the skin of rats or guinea pigs with citrate buffer. The residue, referred to as "kolastromine" does not show the periodic cross-banding of collagen and differs from collagen in histochemical reactions; its X-ray diffraction pattern shows a spacing of 2.9 A. Collagen contains about 80% kolastromine and 20% procollagen. The latter cannot be extracted until an extremely thin covering over the surface of the fibrils is "weakened" by enzyme action. The cross-banding of collagen fibrils is ascribed to a procollagen-polysaccharide complex. Procollagen and kolastromine differ in amino acid makeup but both contain considerable, though different, amounts of hydroxyproline.

H.B.M.

CORRECTION

Through an error the address of G. H. W. Humphreys was published in the February, 1958, issue of the *Journal* as Inchmery, Sabrina Terrace, Thorneloe, Worcester, England. This is incorrect. Mr. Humphreys is still at the same address: c/o Forestal Central Laboratories, Harpenden Rise, Harpenden, Herts., England.

The Keys to Quality

From rugged sole leather to the soft, luxurious leather for gloves, Nopco tanning products insure such characteristics as uniformity, pliability, strength, softness and durability.

For detailed information about Nopco chemical products, plus Nopco research facilities, available to you, simply write to the Tanning Oil Division or consult with the Nopco technical service representative in your area.

Nopco chemicals for the leather industry include:

- Anti-Oxidant and Masking Agents
- Emulsifiers and Penetrants
- Fat Liquors
- Degreasing Agents
- Sponging Compounds
- Specialty Items

NOPCO **VITAL INGREDIENTS FOR VITAL INDUSTRIES**

NOPCO CHEMICAL COMPANY, HARRISON, N.J.

PLANTS: *Harrison, N.J. • Cedartown, Ga. • Richmond, Calif. • London, Canada*

BIOBATE

- biobate is a highly standardized bating compound of extreme stability.
- biobate provides controlled, effective enzyme action during bating for all types of leather.
- biobate is adaptable to all bating conditions and procedures.

SEBACOL

- **for dependable unhairing**

  sebacol produces clean, uniform quality leather under varied beamhouse practices.

STEROZOL

- **reliable germicide**

  sterozol inhibits bacterial action and mold growth on raw stock and leather in process.

WALLERSTEIN COMPANY, INC. • 180 MADISON AVENUE, NEW YORK 16, N.Y.

The Reader Comes First

LEATHER and SHOES believes in the "Golden Rule" of journalism --serves its readers first. It has no "sacred cows" nor prejudices.

Because of this, it is first choice of the industry's key executives. L&S is the most widely read and quoted paper in its field, and leads in paid (audited) circulation, subscription and advertising receipts.

Readers and advertisers benefit most by this policy. That's why its subscription list and advertising indexes read like the Who's Who of the industry.

LEATHER and SHOES

THE MAGAZINE FOR EXECUTIVES

300 West Adams Street
CHICAGO 6, ILLINOIS

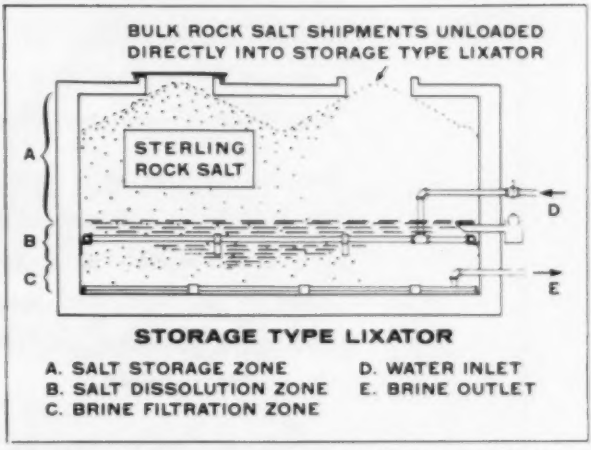
Using Salt Efficiently

by **INTERNATIONAL SALT COMPANY, INC.**

Producing Crystal-Clear Brine at Lowest Cost — by Self-Filtration

Today, more and more industrial companies are using a foolproof brine-making process that produces crystal-clear brine from rock salt, without using supplemental filter beds or other filtering devices. This process takes place in the "Sterling Lixator", a rock-salt dissolver developed exclusively by International Salt Company. The Lixate Brine made in the Lixator is brilliantly clean and clear . . . is excellent for leather dyeing solutions and tanning formulae.

Here, briefly, is how self-filtration works in the Sterling Lixator: A Lixator is filled with Sterling Rock Salt. Water, admitted near the top, dissolves salt as it flows downward. While flowing down, the brine made in this way becomes fully saturated, and can absorb no more salt. Still flowing down, this brine is *completely filtered* by the salt-crystal bed in the bottom portion of the Lixator. Thus, the Lixate Brine drawn off through a discharge pipe at the bottom of the Lixator is clean, pure, and crystal clear.



The Storage Lixator — a combination salt storage tank and dissolving tank.

Other Lixator Advantages.

*The Lixator permits salt storage and brine making at one location most convenient to the point of salt entry *pipes* deliver brine to points of use.

*This piping feature eliminates the work of moving dry salt from storage piles to other plant locations. It permits substantial savings in labor.

*The Lixator *automatically* controls salt feed, water feed, and brine discharge. Rapid, uniform brine production is maintained constantly, because in the Lixator there is no bridging, caking or channeling.

Many types of Lixators are available from International Salt Company. There are Storage Lixators, Silo Lixators and Sterling Model Lixators — in numerous designs to suit any plant layout. And every Lixator operates on the economical self-filtration principle.

For expert advice on the particular Lixator type that will do the best job for you, phone or write the nearest district sales office, or write to us direct. One of our sales engineers will gladly show you how this remarkable brine-making equipment can save you money in leather tanning operations.

SALES OFFICES: Atlanta, Ga.; Chicago, Ill.; New Orleans, La.; Baltimore, Md.; Boston, Mass.; Detroit, Mich.; St. Louis, Mo.; Newark, N. J.; Buffalo, N. Y.; New York, N. Y.; Cincinnati, O.; Cleveland, O.; Philadelphia, Pa.; Pittsburgh, Pa.; Memphis, Tenn.; and Richmond, Va.

Service and research are the extras in **STERLING SALT**

PRODUCT OF INTERNATIONAL SALT COMPANY, INC.

COLUMBIA-SOUTHERN full-line supplier of quality-controlled chromates. **SODIUM BICHROMATE** Orange-red, deliquescent crystalline material. Available as Liquid (70% solution) in 8,000 gallon tank cars and tank trucks; as Granular in 400 lb. fiber drums and 100 lb. paper bags. **SODIUM CHROMATE** Yellow, anhydrous powder. Available in 200 lb. fiber drums and 100 lb. paper bags. **POTASSIUM BICHROMATE** Red-orange, crystalline material. As Granular or Powder in 400 lb. fiber drums and 100 lb. paper bags.

COLUMBIA-SOUTHERN CHEMICAL CORPORATION A Subsidiary of Pittsburgh Plate Glass Co.

One Gateway Center, Pittsburgh 22, Pennsylvania • DISTRICT OFFICES: Cincinnati, Charlotte, Chicago, Cleveland, Boston, New York, St. Louis, Minneapolis, New Orleans, Dallas, Houston, Pittsburgh, Philadelphia, San Francisco • IN CANADA: Standard Chemical Limited

1st CHOICE

for Higher Quality Leather Production

L.H. LINCOLN & SON, INC. LINCO PRODUCTS COUDERSPORT, PA.

Better Grading Figures!
Better Cutting Figures!
Overall Economy!

Extracts — Pancreatic Bates — Fillers
Sole Leather Finishes - Tanners Sugar
Tanners Lime — Chemicals

L.H. LINCOLN & SON, INC.
COUDERSPORT, PA.

you can't beat our

SODIUM SULPHIDE

or

SODIUM SULPHYDRATE FLAKES

for Unhairing Qualities

KNOCKDOWN

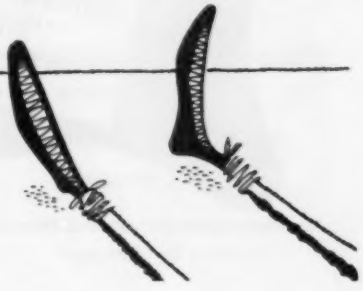
your soaking time with our

SODIUM TETRASULPHIDE

and get more uniform quality -- higher yield

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON, WEST VIRGINIA



MORITE BRAND

EST. 1908

MORITE BRAND

Sulphonated and Compounded

OILS

MORITE BRAND

EST. 1908

WHITTEMORE-WRIGHT COMPANY, INC.

62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

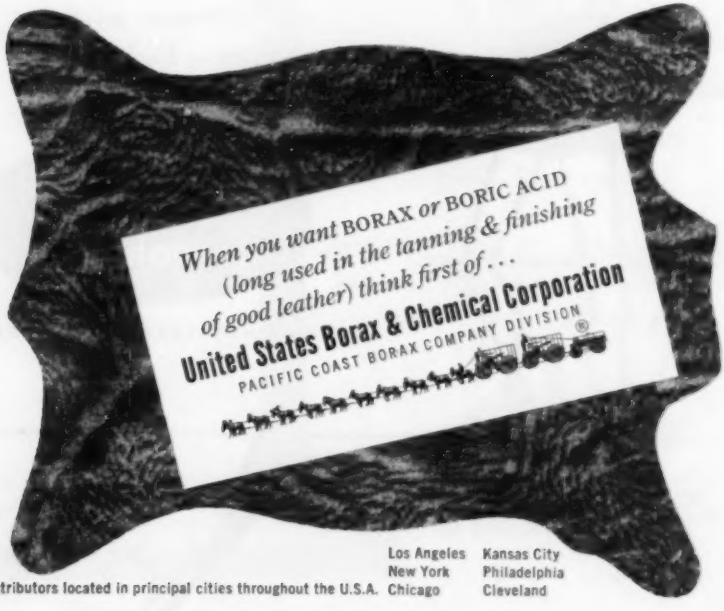
PRESTO

The Original Dry Color
for Splits and Suede
(also in paste form)

PRESTO COLOR COMPANY

WEST ALLIS 14, WIS.

Dry Colors ❖ ❖ Finishes


When you want BORAX or BORIC ACID
(long used in the tanning & finishing
of good leather) think first of . . .
United States Borax & Chemical Corporation
PACIFIC COAST BORAX COMPANY DIVISION

Distributors located in principal cities throughout the U.S.A.

Los Angeles Kansas City
New York Philadelphia
Chicago Cleveland

THOROUGH TANNING IN LESS TIME

Numerous tanners and finishers report that Sun Leather Process Oils make their processing fast and easy because they mix easily, act fast, provide uniform fiber lubrication. Sun Leather Process Oils do not form surface scum...tannage is thorough and even...leathers are stronger and better looking.

For details, prices and delivery information, call your nearest Sun representative or write to...

INDUSTRIAL PRODUCTS DEPARTMENT

SUNOCO

SUN OIL COMPANY

PHILA. 3, PA. • SUN OIL COMPANY LIMITED, TORONTO & MONTREAL

© Sun Oil Company

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

RACINE, WISCONSIN

92 South St., Boston, Mass., Day Gormley Leather Co. 29 W. 36th St., New York City, Eugene Williams
1358 S. Hill St., Los Angeles 15, Calif., David V. Whiting Co.

THE OHIO LEATHER CO.

Quality Calf Leather

LUXOR - BLACK JETTA
KAFFORITE - KOZY - JILL JETTA
EMBOSSED CALF - WHITE WASHETTE

TANNERY AND GENERAL OFFICES:
GIRARD, OHIO
BOSTON - NEW YORK - ST. LOUIS - CHICAGO

THE ORTHMANN LABORATORIES INC.

AUG. C. ORTHMANN, Pres.

Consulting, Analytical and Research Chemists

407 E. MICH., MILWAUKEE, WIS.
Phone: BROADWAY 6-6426-27

CALOPHYL C-10

- Penetrates to the center, exhausting the fat liquor with it.
- Adds weight and plumpness. Does not lay on surface or wash out.
- Dissolves instantly in tap water.
- Compatible over a wide pH range.
- ALSO excellent as a sealer in the base coat and for grinding pigments.

APEX CHEMICAL CO. INC.

Manufacturers since 1900

200 South First St. Elizabethport 1, N. J.

LEATHER
YESTERDAY - TODAY - ALWAYS!

QUALITY EXTRACTS
FOR SEVENTY YEARS

AMEREX PRODUCTS

DERMABATE

LIQUID VEGETABLE EXTRACT BLENDS

Every Type of Extract
for each individual tannery need

ALL OUR BLENDS CONSIST OF
ONLY PURE VEGETABLE EXTRACTS

AMERICAN EXTRACT CO.
PORT ALLEGANY, PA.

Manufacturers of the Largest Variety of
Vegetable Tanning Extracts made in U. S. A.
From Domestic and Foreign Barks

BARRENTAN

B

TESTING AND RESEARCH
CORPORATION
PORT ALLEGANY, PENNA.
ESTABLISHED 1950

PROGRESS WITH LEATHER through BARRENTAN

Compounds - Chemicals - Powdered Tanning Materials
Absebyde Resins - Wheeling Resins

I-2-3

REILLY-
WHITEMAN-
WALTON CO.

OILS of CHARACTER

CONSHOHOCKEN, PA.

THE LEATHER MANUFACTURER

ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER

NEW YORK OFFICE
134 Nassau St.

BOSTON OFFICE
683 Atlantic Ave.

Warner

BELL-MINE LIME

Accurate laboratory control assures you of consistently better milk of lime.

You can depend on Warner Bell-Mine Lime for uniform purity, analysis and physical properties.

WARNER COMPANY, Bellefonte Division, Bellefonte, Pa.
Philadelphia Pittsburgh

Mardol
TANNERY OILS

TANNERY OILS
AND FAT LIQUORS
FOR ALL TYPES OF LEATHER

MARDEN-WILD CORPORATION
500 COLUMBIA STREET, SOMERVILLE, MASS.
MARDEN-WILD OF CANADA LTD., HALIFAX, N. S.

Salem Oil & Grease Co.

FAT LIQUORS
FEATURING
CONTROLLED PENETRATION

•

SALEM, MASSACHUSETTS

finest products fastest service

EST. 1924

TANNING EXTRACTS
SULFONATED OILS
STUFFING GREASES
LIGNOSULFONATES

ARTHUR C. TRASK CO.

- CABLE: *Actrask*
- TELETYPE: CG1478

327 So. La Salle St. Chicago 4, WAbash 2-8900
55 W. 42nd St. New York 36, LOngacre 4-8489

STANDARD HIDE POWDER

A material made to specifications and used internationally for the analysis of vegetable tanning materials

FRANK F. MARSHALL
RIDGWAY · PENNSYLVANIA

KEPECO FINNALINE KEPOLAC
EMULLO KEEPA-SHINE FONDO
UNI-LAK
(Reg. U. S. Pat. Office)

KEPEC CHEMICAL CORPORATION
MILWAUKEE 1, WISCONSIN

Garden State Tanning Inc.
Pine Grove, Pa.

Manufacturers of
Upholstery Leather

New York Office **330 Fifth Avenue**

"The Extension of Knowledge is by the Investigation of Matter".

This space dedicated to
Tanner's Council Research Laboratory
by a Friend

LEATHER and TANNING MATERIALS

CONSULTING • TESTING • RESEARCH • DEVELOPMENT
for the
TANNING AND ALLIED INDUSTRIES

Specialists: Sampling and Testing of Tanning Materials

UNITED STATES TESTING COMPANY
INCORPORATED
1950 Park Avenue, Hoboken, N. J.

Finishes
for all types of
Leather

FINE LEATHER FINISHES — NLF

NEWARK
LEATHER FINISH CO.

8 WILHELM ST. HARRISON, N. J.
Telephone HUmboldt 2-5072

by

THE AULSON *Tanning Machinery Co.*

Main Office and Factories at Beverly, Mass. ★ Branch Office under direction of E. R. Aulson, Waukegan, Ill.

JOHNSON AND CARLSON

We Manufacture and Install

DRUMS - VATS - PADDLES - WOOD TANKS

Suppliers of V-Belts, Sprockets, Motors, Chain and Other Tannery Equipment

848 EASTMAN ST., CHICAGO 22, ILL.

NEW CHROMIUM COMPOUNDS
for the Progressive
TANNING CHEMIST

NUCHROME

Pure Basic Chromic Sulfate. No impurities, no sodium, aluminum or other salts.

DRY (35% Cr_2O_3)

LIQUID (25% Cr_2O_3)

CHROMIC CHLORIDE
CHROMIC ACETATE
CHROMIC FORMATE
CHROME ALUM AND OTHERS

FIBER CHEMICAL CORPORATION

P. O. BOX 218 MATAWAN, N. J.

A. W. HOPTON

- Leather processes, Treatments
- Experimental Tannage Facilities
- Testing: Wear, Heat, Water Resistance, etc.
- Consulting — Research

Office — Lab, 19th St.
NIAGARA FALLS, N. Y.

E. F. DREW & CO., INC.

BOONTON, N. J.

MANUFACTURERS OF
LEATHER OIL PRODUCTS

BORNEO CUTCH EXTRACT
(MANGROVE BARK EXTRACT)

SAXE CUTCH CORPORATION
500 FIFTH AVE., NEW YORK 36, N.Y.

CALGON* Pre-Tan

the tanning time saver that produces better leather

Calgon Pre-Tan cuts tanning time to one-third or one-fourth the normal time when it is used before vegetable tanning. This is because Calgon's quick action speeds up the penetration of vegetable liquors, hastening the tanning process.

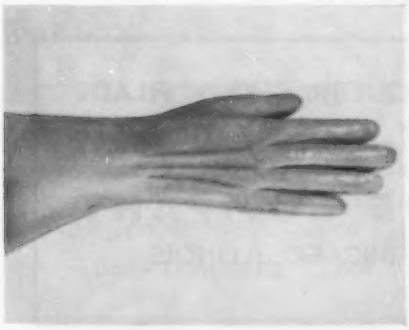
Besides being a time and money saver, Calgon adds to the quality of leather. Calgon's dispersive action and ability to combine with proteins produce tanned leather that's exceptionally free from stains, has a dense grain structure, and a long silky fiber that contributes greatly to tensile strength.

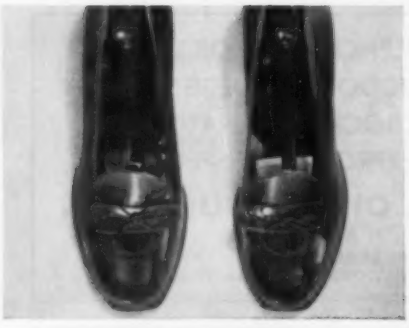
For high quality leather and faster tanning, try Calgon Pre-Tan. Write now for your free copy of "Calgon Data for the Leather Chemist."

*Calgon is the Registered Trademark of Calgon Company for its glassy sodium phosphate products.

CALGON COMPANY

DIVISION OF HAGAN CHEMICALS & CONTROLS, INC.
HAGAN BUILDING, PITTSBURGH 30, PENNSYLVANIA
DIVISIONS: CALGON COMPANY, HALL LABORATORIES
IN CANADA: HAGAN CORPORATION (CANADA) LIMITED, TORONTO





for uniformity in Chrome Tanning specify dependable

MUTUAL SODIUM BICHROMATE

When you use Mutual Sodium Bichromate in the preparation of your chromic tanning bath you can be confident that there will be dependable consistency in its traditional high quality. The unvarying high purity of Mutual's product eliminates the possibility of bichromate problems in liquor formulations. This is assured by Mutual's rigid continuous quality control testing during manufacture.

Remember, too, that Mutual technical service, backed by over 100 years of manufacturing experience, is available to you when you need it—from America's *first* producer of chromium chemicals.

For those who want a *prepared* one-bath chrome tan of assured uniformity, Mutual supplies KOREON in two types—KOREON M at 33-35% basicity and KOREON X at 50-52% basicity.

Mutual Chromium Chemicals

MUTUAL

Sodium Bichromate
Sodium Chromate
Chromic Acid

Potassium Bichromate
Potassium Chromate
Ammonium Bichromate

Koreon (One-Bath Chrome Tan)

MUTUAL CHROMIUM CHEMICALS
SOLVAY PROCESS DIVISION
Allied Chemical & Dye Corporation
61 Broadway, New York 6, N. Y.

Allied Chemical

Please send:

- ☐ Bulletin No. 107—"Preparing Basic Chromic Sulfate Tanning Liquors from Sodium Bichromate"
- ☐ Bulletin No. 108—"Analytical Methods for Bichromate Reduction Control"
- ☐ Booklet No. 54 – "KOREON One-bath Chrome Tan for Leather"

DEPT. 5

NAME_____

POSITION_____

COMPANY_____

STREET_____

CITY_____ ZONE____ STATE_____

"ADE II AN" GAMBADE
LIQUID QUEBRACHO EXTRACT
FILADE DRIPASTE

THE TANNADE COMPANY
2136 DOMINICK ST., CHICAGO, ILLINOIS

THE STAMP OF VORTEXOL DEPENDABILITY

SULPHONATED OILS and FATLIQUORS — SUEDE SPRAYS
CROCK ELIMINATORS
WATERPROOFING SPECIALTIES

EASTERN INDUSTRIAL OIL PRODUCTS CO.
SAUGUS, MASS.
EASTERN OIL OF MEXICO PASEO DE LA REFORMA 95 MEXICO DF
EXPORT AGENT: WOLFF—INTERNATIONAL, Milwaukee, Wisconsin

Proctor **EQUIPMENT** for the **TANNING INDUSTRY**

- ROTO-SPRAY (4 or 8 Gun)
- PASTED LEATHER DRYERS
- TOGGLE DRYERS
- POLE AND HOOK TYPE CONVEYOR DRYERS
- SEASONED SKIN AND SPRAYED FINISH DRYERS
- WASHED CATTLE HAIR DRYERS

PROCTOR & SCHWARTZ, INC. Philadelphia 20, Pa.
LUCIEN BUCK EXCLUSIVE SALES REPRESENTATIVE FOR THE LEATHER INDUSTRY

CONSULTING SERVICE

Technical consultation is available for improving your leather, reducing your costs and developing new leathers and finishes. More than 40 years practical application of Scientific Research to Leather manufacturing.

ADOLF SCHUBERT, 549 W. Washington Blvd., CHICAGO, ILL.

Solvent Tannage,
born of Science is
a chemical Process
Industry — Be Prepared

Fred O'Flaherty

THE TANNERS' COUNCIL
RESEARCH LABORATORY
University of Cincinnati

We serve the Tanning and Leather Industry through a broad program of Research.

BONA ALLEN, INC.

Buford, Georgia

TANNERS SINCE 1873

•

Finest English Rein
and Strap Leather

Latigotan Harness Leather

Manufacturers of genuine English type and full rigged hand tooled roping saddles.

HOWES LEATHER CO. INC.

SOLE LEATHER

•

SIDE LEATHER

•

Tanners Cut Sole Division

•

CUT SOLES

BOSTON, MASS.
ST. LOUIS, MO. CHICAGO, ILL.

INDEX TO ADVERTISERS

ADOLF SCHUBERT XXXVII
AMERICAN EXTRACT CO. XXVIII
APEX CHEMICAL CO., INC. XXVIII
ARKANSAS COMPANY, INC. VI
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XVIII
ATLAS REFINERY XIV
AULSON TANNING MACHINERY CO., THE XXXIII
A. W. HOPTON XXXIV
BARKEY IMPORTING CO., INC. XII
BARRENTAN CORPORATION XXVIII
BARIUM REDUCTION CORPORATION XXV
BONA ALLEN, INC. XXXVII
BUCKMAN LABORATORIES, INC. IV
CHEMTAN COMPANY ..... Outside Back Cover
COLUMBIA-SOUTHERN CHEMICAL CORP. XXIII
EASTERN INDUSTRIAL OIL PRODUCTS CO. XXXVI
E. F. DREW & CO., INC. XXXIV
EISENDRATH TANNING CO. XXVII
EUROPEAN CHESTNUT MFG'S ASSO. V
FIBER CHEMICAL CORPORATION XXXIII
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING, INC. XXXI
GEIGY COMPANY, INC. IX
GENERAL DYESTUFF COMPANY ..... X — XI
HAGAN CHEMICALS & CONTROLS, INC. XXXIV
HOOKER ELECTROCHEMICAL CO. XIII
HOWES LEATHER CO., INC. XXXVII
INTERNATIONAL SALT CO., INC. XXII
JOHNSON AND CARLSON XXXIII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXI
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. XXIV
MARDEN-WILD CORPORATION XXX
MUTUAL CHROMIUM CHEMICALS, ALLIED CHEMICAL & DYE CORP. XXXV
NEWARK LEATHER FINISH CO. XXXII
NOPCO CHEMICAL CO. XIX
OHIO LEATHER CO., THE XXVII
OLSON IMPORTING COMPANY, INC., THE ..... Inside Front Cover
ORTHMANN LABORATORIES, INC., THE XXVII
PRESTO COLOR CO. XXVI
PROCTOR AND SCHWARTZ, INC. XXXVI
REILLY-WHITEMAN-WALTON CO. XXIX
ROBESON PROCESS CO. II
ROHM & HAAS VIII
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXXIV
SEABOARD CHEMICALS, INC. ..... Inside Back Cover
SOCONY MOBIL OIL CO., INC. XVII
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XV
SUN OIL COMPANY XXVII
TANIMEX CORPORATION III
TANNADE COMPANY XXXVI
TANNER'S COUNCIL RESEARCH LABORATORY ..... XXXI — XXXVII
UNITED STATES BORAX & CHEMICAL CORP. XXVI
UNITED STATES TESTING COMPANY XXXII
WALLERSTEIN COMPANY, INC. XX
WARNER CO. XXX
WHITTEMORE-WRIGHT CO. XXVI
WOLF, JACQUES & CO. VII
YOUNG CO., J. S. XVI

Split Suede Tanner Colors Directly From The Blue With Synova, Gets Short Silken Nap

Some months ago a progressive eastern split suede tanner wanted to color directly from the blue. But conventional sulfated oils gave him a sheeny buffing job and poor unlevel coloring.

Hearing about Synova and its success on suedes, he made a trial run —following suggestions offered by a Seaboard representative. The results were surprisingly good. So he followed with a full pack—and is now fatliquoring his entire production with Synova.

Stock Upgraded on Table

Coloring directly from the blue, he now produces a low-cost sueded split. And even though his suedes are pasted under fast drying conditions, they are properly lubricated and conditioned—and buff beautifully to a short resilient silken nap. Coloring is improved and much leveler.

By using this fast inexpensive process, he produces a better suede at lower cost. Takes a higher profit margin too. By eliminating pearling, he increases production, using the same equipment.

Also he reports a number of other benefits from using Synova. It is absolutely uniform, has long storage stability, and its odor is clean and pleasant.

Try a Sample Yourself

What about you? Whether you're tanning calf or kid suede, sueded reversible sides or splits, wouldn't it be a good idea to see for yourself what Synova can do for your suedes? Prove what other salesminded tanners are saying — that for pearling, coloring directly from the blue or grain clearing, modern Synova is the finest discovery they ever made. We'd like to send you a trial sample. Write or phone today.

It's time you switched to Synova!

SEABOARD CHEMICALS, INC.

Dept. 4A, 30 Foster St.

Salem, Massachusetts

In Canada: Tennant Union, Ltd., Toronto

Overseas Export: Wolff International, Inc., Milwaukee, Wisconsin, U. S. A.

Mulling over an idea...

Exchanging ideas and considering both the practical and chemical aspects is the first step in planning new products — thoughts preceding the deed. Once we have decided on a plan of action our research department takes over to bring this idea to life.

CHEMTAN COMPANY

EXETER, NEW HAMPSHIRE

All our facilities are devoted exclusively to the tanning industry

CHEMTAN COMPANY
EXETER, NEW HAMPSHIRE